



# Atomic-Scale Probing the Priority of Oxidation Sites of an Organic Molecule Adsorbed at the Cu–O/Cu(110) Interface

Kai Sheng,<sup>[a]</sup> Huihui Kong,<sup>[a]</sup> Zhiwen Li,<sup>[b]</sup> Chi Zhang,<sup>[a]</sup> Qiang Sun,<sup>[a]</sup> Qinggang Tan,<sup>[a]</sup> Yunxiang Pan,<sup>[a]</sup> Aiguo Hu,<sup>\*,[b]</sup> and Wei Xu<sup>\*,[a]</sup>

Catalytic reactions occurring on oxide-supported Cu and Cu-supported oxide catalysts are of fundamental interest in both industrial and scientific fields. Though the interface between Cu and oxide species has been regarded as the reaction site, the exact role of the interface in the catalytic reactions is not fully understood yet. In this work, by using a model system including Cu–O chains supported on Cu(110) and an organic molecule with alkynyl and aldehyde groups, we attempted to obtain a fundamental understanding of the role of the inter-

face in the catalytic reactions. A combination of high-resolution scanning tunneling microscopy imaging and density functional theory calculations provided direct evidence at the atomic scale that the interface between the Cu–O chains and the Cu(110) surface is the most favorable site for the adsorption and activation of organic molecules, and the oxygen of Cu–O has an activity to oxidize both the alkynyl and aldehyde groups of the molecules adsorbed at the interface.

## Introduction

Oxide-supported Cu and Cu-supported oxide catalysts have been found as among the most active materials in a wide range of reactions, such as oxidation of hydrocarbons, CO, and aldehyde.<sup>[1]</sup> In some reactions, the supported Cu-based catalyst can even substitute the expensive noble metal catalysts, owing to its high catalytic activity.<sup>[1f]</sup> Supported catalysts are generally more active than the individual components of the catalysts, which is attributed to the presence of the interface between the support and the supported species.<sup>[1f,2]</sup> For example, CeO<sub>x</sub> supported on Cu(111) exhibits strongly enhanced catalytic activity relative to Cu(111) for the CO oxidation reaction at the same conditions, which was explained by the formation of active species (e.g., Cu<sub>2</sub>O<sub>1+x</sub>) at the interface of CeO<sub>x</sub>/Cu(111).<sup>[1f]</sup> Though the interface was suggested to be the reason for the high activity of the supported catalyst, the exact role of the interface in the catalytic reactions has not been fully understood yet. It is therefore of utmost importance to

explore the role of the interface in the reactions under ultra-high vacuum conditions to provide atomic-scale insight into the fundamental question of how the Cu-based catalysts may work under real catalytic conditions.


Oxide chains/clusters growing on metallic surfaces are a suitable system to study the interface between metal and oxide species. Herein, by choosing a model system including Cu–O chains supported on the Cu(110) surface and an organic molecule (4-(2-ethynylphenyl)-ethynyl benzaldehyde, EBA) with three different kinds of functional groups: aldehyde, terminal alkynyl, and nonterminal alkynyl (as shown in Figure 1a, inset), we attempted to explore the role of the interface between the Cu–O species and the Cu surface in catalytic reactions. A combination of high-resolution scanning tunneling microscopy imaging and state-of-the-art DFT calculations provided direct evidence at the atomic scale that the interface of Cu–O/Cu(110) is the most favorable site for the adsorption and activation of the EBA molecule, and the oxygen of Cu–O has an activity to oxidize both the alkynyl and aldehyde groups of the EBA molecules adsorbed at the interface. Moreover, the alkynyl group was found to be oxidized more facile than the aldehyde group as the interaction between the alkynyl group and Cu–O is thermodynamically more favorable. These findings may help to elucidate the key factors affecting the selectivity and activity of Cu-based catalysts.

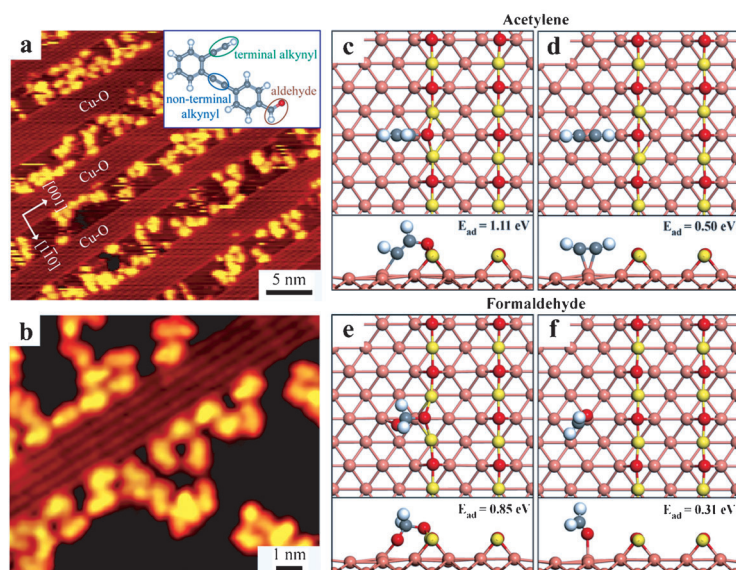
## Results and Discussion

After deposition of EBA molecules on Cu–O/Cu(110) at room temperature (RT), we found that the molecules predominantly adsorbed either on the bare copper surface regions or at the interface of Cu–O/Cu(110) as depicted in Figure 1a. No mole-

[a] K. Sheng, H. Kong, C. Zhang, Q. Sun, Dr. Q. Tan, Dr. Y. Pan, Prof. Dr. W. Xu  
College of Materials Science and Engineering  
Key Laboratory for Advanced Civil Engineering Materials  
(Ministry of Education)  
Tongji University  
Caoan Road 4800, Shanghai 201804 (P.R. China)  
Fax: (+86)21-69582148  
E-mail: xuwei@tongji.edu.cn

[b] Z. Li, Prof. Dr. A. Hu  
School of Materials Science and Engineering  
Shanghai Key Laboratory of Advanced Polymeric Materials  
East China University of Science and Technology  
Meilong Road 130, Shanghai 200237 (P.R. China)  
E-mail: hagamhsn@ecust.edu.cn

 Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/cctc.201200955>.



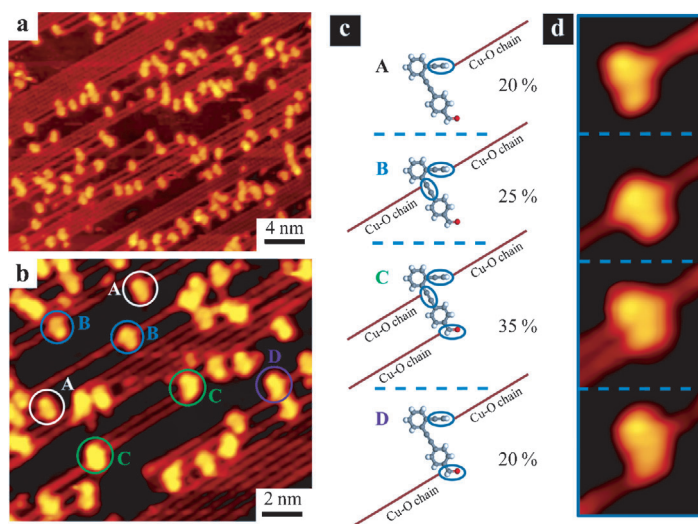
**Figure 1.** a) STM image recorded after deposition of EBA molecules on Cu–O/Cu(110) at RT ( $I_t = 0.58$  nA;  $V_t = 1250$  mV;  $T = 253$  K). The Cu–O regions are indicated in the image. Inset: the ball-and-stick model of an EBA molecule, its three functional groups are indicated with ellipses. b) Close-up STM image showing the adsorption geometry of an EBA molecule at the single-molecule level ( $I_t = 0.40$  nA;  $V_t = 2102$  mV;  $T = 253$  K). DFT-optimized structures of the adsorption of c, d) acetylene and e, f) formaldehyde on Cu–O (parts c, e) and the bare Cu(110) surface (parts d, f). Oxygen atoms are shown in red, copper atoms of Cu–O in yellow, copper atoms of the Cu(110) surface in brown, carbon atoms in grey, and hydrogen atoms in white.

cule was found to be located on the top of the Cu–O regions at RT, even at high coverage. This suggests that binding of the EBA molecule on the top of the Cu–O chains is much weaker than that at the bare copper surface and the interface of Cu–O/Cu(110). The close-up STM image (Figure 1b) reveals at the single-molecule level that there was no long-range well-ordered structure formed on the bare copper surface, and at the interface the molecules mainly adsorbed with their long axes parallel to the growth direction of Cu–O chains, in a peanut-like configuration. The molecules were stable on the surface even at RT and most of them adopted a uniform configuration at the interface of Cu–O/Cu(110), suggesting that there is a relatively strong binding between the molecule and the substrate. By carefully analyzing the adsorption geometry of the EBA molecule and comparing it with the molecular model, we speculated that the interaction between the molecule and the Cu–O/Cu(110) occurs most likely through the terminal alkynyl group. To verify this hypothesis and work out the corresponding atomic-scale model for the adsorption structure, DFT calculations were performed on several models. In the calculations we simplified the EBA molecule and singled out the acetylene and formaldehyde as the models to explore the interactions between the alkynyl and aldehyde groups and the Cu–O/Cu(110).

In Figure 1c and 1d, the two most stable adsorption configurations of acetylene on the interface of Cu–O/Cu(110) and on the bare Cu(110) surface are shown, respectively. Figure 1c reveals that one of the carbon atoms of acetylene interacts with an oxygen atom of the Cu–O chain with a distance of  $1.40 \text{ \AA}$ ,

and the oxygen atom is relaxed upward by  $0.82 \text{ \AA}$ . Figure 1d reveals that the acetylene binds only to a copper atom of the surface. The calculated adsorption energies of acetylene corresponding to these two configurations are  $1.11 \text{ eV}$  and  $0.50 \text{ eV}$ , respectively. In Figure 1e and 1f the two most stable adsorption configurations for formaldehyde on the interface of Cu–O/Cu(110) and on the bare Cu(110) surface are shown, respectively. Similarly to the scenario for acetylene, Figure 1e reveals that the carbon atom of formaldehyde interacts with an oxygen atom of the Cu–O chain with a distance of  $1.45 \text{ \AA}$ , and the oxygen atom is relaxed upward by  $0.79 \text{ \AA}$ . In Figure 1f it is shown that the formaldehyde binds only to a copper atom of the surface. The calculated adsorption energies of formaldehyde corresponding to these two configurations are  $0.85 \text{ eV}$  and  $0.31 \text{ eV}$ , respectively. The adsorbed acetylene and formaldehyde molecules are found to be largely distorted from their gas-phase configurations indicating that the molecules have been activated. According to the DFT calculations we can draw the conclusion that the EBA molecule prefers to interact with the oxygen atom of Cu–O/Cu(110) through its terminal alkynyl group, which is in good agreement with the STM findings. Because of the steric hindrance, the interaction with the Cu–O/Cu(110) through the nonterminal alkynyl group is less facile at this adsorption geometry.

Note that the Cu–O chains were intact after deposition of the EBA molecules as shown above; however, surprisingly, after annealing the sample at  $370 \text{ K}$  for  $10 \text{ min}$ , some of the Cu–O chains were found to be partially broken and incomplete along the growth direction and terminated by the molecules. The interstitials between the Cu–O chains were somewhat enlarged with the molecules embedded as shown in Figure 2a. Now almost all of the molecules interacted with the Cu–O chains and molecules are no longer found on the bare surface. To gain further insight into this novel phenomenon, a thorough and detailed analysis of the STM images was conducted at the submolecular scale. High-resolution close-up STM images helped disclose the scenario of the interaction between the EBA molecules and the Cu–O chains. Basically, there are four binding modes for the molecule (through different functional groups) to bind to the Cu–O chains. The characteristic examples of such four binding modes are marked in Figure 2b with **A**, **B**, **C**, and **D**. In Figure 2c these four modes are illustrated schematically, and in Figure 2d the close-up STM images corresponding to the four modes with submolecular resolution are shown to identify the binding configurations. The registry between the molecules and the Cu–O chains in these four modes was demonstrated by overlapping the atomic lattice of the Cu(110) surface as shown in the Supporting Information (Figure S1). According to the STM images and in comparison to the molecular model we attributed mode **A** to the interaction between the terminal alkynyl group of the EBA molecule and a single Cu–O chain. Likewise, we attributed the interactions between the terminal alkynyl and nonterminal



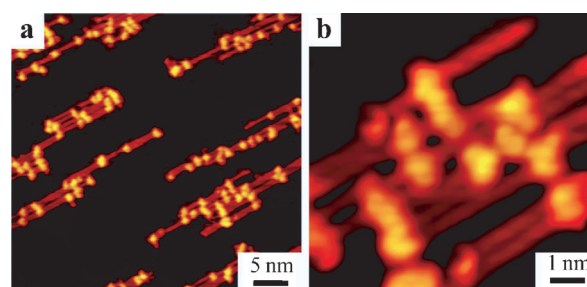
**Figure 2.** a) STM image recorded after annealing the sample at 370 K for 10 min. ( $I_t = 0.72$  nA;  $V_t = 1250$  mV;  $T = 263$  K). b) High-resolution close-up STM image revealing the scenario of the interaction between the Cu–O chains and the EBA molecules. Examples of the four binding modes are marked with A, B, C, and D, respectively ( $I_t = 0.57$  nA;  $V_t = 1250$  mV;  $T = 263$  K). c) Schematic illustrations of the four binding modes and the statistics of their occurrences in the counted images. d) Close-up STM images corresponding to the four interaction modes.

alkynyl groups and two Cu–O chains to mode B; the terminal alkynyl, nonterminal alkynyl, and aldehyde groups and three Cu–O chains to mode C; the terminal alkynyl and aldehyde groups and two Cu–O chains to mode D. Most of molecules adjusted their orientations with the long axes perpendicular to the growth direction of the Cu–O chains. Owing to the break of the Cu–O chains, the steric hindrance thus disappeared with respect to the nonterminal alkynyl group, therefore, this functional group also participated in the formation of mode B and C. We also performed a statistical analysis on these four interaction modes in a series of STM images and the percentages of occurrence for mode A, B, C, and D were 20, 25, 35, and 20%, respectively, with errors of  $\pm 2\%$ . This finding indicated that after annealing the sample at 370 K, the adsorbed molecules had a slight preference for interaction with the broken Cu–O chains in the mode C, the other three modes had almost the same probabilities.

Interestingly, after further annealing the sample at 420 K for 10 min, we found that the number of Cu–O chains decreased significantly and the Cu–O chains became more and more incomplete as shown in Figure 3a. A close-up STM image revealed that the molecules bound to the remaining few Cu–O chains similarly to those in the previous step, and now most of the molecules interacted with the Cu–O chains through all three functional groups as shown in Figure 3b. Continuous anneal at 470 K for 10 min led to the complete disappearance of short Cu–O chains together with molecules and resulted in a clean Cu(110) surface (not shown). Considering that our experiments are performed under ultrahigh vacuum conditions and no additional  $O_2$  was present in the system, it is not surprising that the Cu–O chains disappeared gradually with the oxidation reaction of the adsorbed EBA molecules with the

oxygen atoms of the Cu–O proceeding. The above DFT calculations suggested that the oxygen site of Cu–O is favorable for adsorption of the molecule. After adsorption, the oxygen atoms of Cu–O are relaxed upward and the adsorbed molecules are activated. Therefore, if enough energy is provided, the oxygen atoms will be abstracted by the adsorbed molecules, in other words, the molecules will be oxidized by the oxygen atoms. Thus, breakage of Cu–O chains at elevated temperatures is very likely to be attributed to the abstraction of the oxygen atoms by the adsorbed molecules, and the final reaction products of EBA molecules with the oxygen atoms will desorb from the surface at higher temperatures, causing disappearance of the Cu–O chains. These results are in good agreement with results by other studies that the lattice oxygen atoms participated in activating the molecules adsorbed on copper oxide.<sup>[3]</sup>

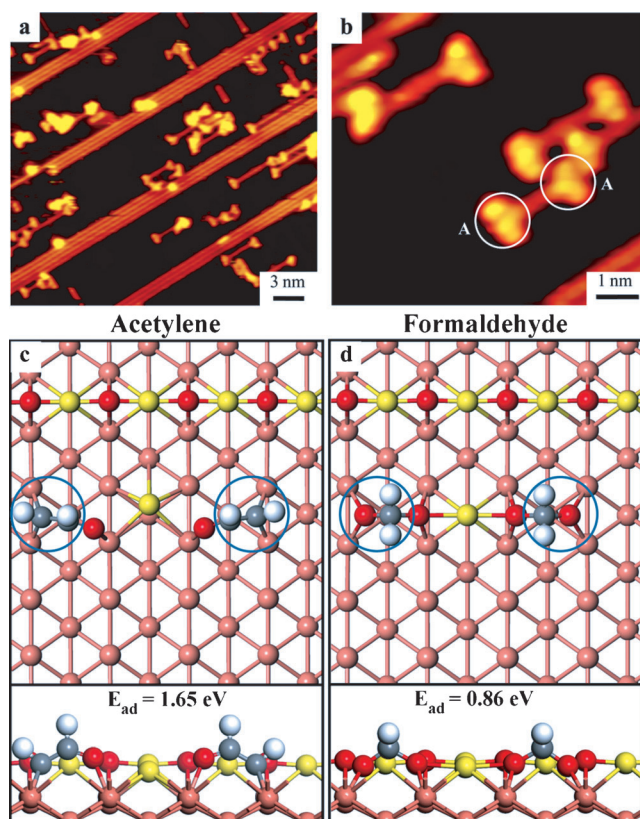
To obtain further fundamental insight into the priority of the oxidation sites of the EBA molecule, we performed the experiment in a further step with a low-coverage molecular deposition. It was seen that after annealing the sample at 370 K, the molecules predominately interacted with the single Cu–O



**Figure 3.** a) STM image recorded after further annealing the sample at 420 K for 10 min ( $I_t = 0.61$  nA;  $V_t = 1250$  mV;  $T = 273$  K). b) Close-up STM image revealing that most of the EBA molecules interacted with the Cu–O chains through all three functional groups ( $I_t = 0.58$  nA;  $V_t = 1250$  mV;  $T = 273$  K).

chains as shown in Figure 4a. In the close-up STM image it is shown that most of the molecules interact with single Cu–O chains in mode A, that is, the molecule preferentially interacts with the Cu–O through the terminal alkynyl group (Figure 4b). Furthermore, we performed DFT calculations to model the scenario of the interactions between acetylene and formaldehyde and a broken Cu–O chain as shown in Figure 4c and 4d, respectively. As the oxygen sites of Cu–O were demonstrated to be the favorable sites for the interaction of acetylene and formaldehyde with Cu–O chains, the oxygen atoms in these two models are considered to be used as the termini of Cu–O chains. The model in Figure 4c shows that the interactions of acetylene molecules with the termini of Cu–O chains result in a cleavage of the Cu–O bonds. The structural change of Cu–O chains induced by the interactions with formaldehyde molecules is, however, moderate as shown in Figure 4d. The binding energies for acetylene and formaldehyde with the broken





**Figure 4.** a) STM image recorded after annealing the sample at 370 K for 10 min ( $I_t = 0.43$  nA;  $V_t = 1250$  mV;  $T = 243$  K). b) Close-up STM image revealing that most of the EBA molecules interacted with single Cu–O chains in mode A. ( $I_t = 0.41$  nA;  $V_t = 1250$  mV;  $T = 243$  K). DFT calculations demonstrating that c) acetylene is energetically more favorable than d) formaldehyde to adsorb at the terminus of the broken Cu–O chain (with oxygen). Oxygen atoms are shown in red, copper atoms of Cu–O in yellow, copper atoms of the Cu(110) surface in brown, carbon atoms in grey, and hydrogen atoms in white.

Cu–O chains were calculated to be 1.65 eV and 0.86 eV per molecule, respectively; these values are stronger than those for the interactions of acetylene and formaldehyde with intact Cu–O chains (as shown in Figure 1c and 1e). Two tentative conclusions can be drawn from the DFT calculations: First, compared to the intact Cu–O chains, broken Cu–O chains have a higher activity toward the adsorption and activation of acetylene and formaldehyde molecules because of the occurrence of new interfaces. Second, the terminal alkynyl group of the EBA molecule has a higher priority than the aldehyde group for oxidation by the oxygen atoms of Cu–O because for acetylene a stronger interaction with the Cu–O chain has been shown.

## Conclusions

In summary, by combining the high-resolution ultrahigh-vacuum STM imaging and state-of-the-art DFT calculations, we have gained direct evidence at the atomic scale that the interface of Cu–O/Cu(110) is the most favorable site for the adsorption and activation of 4-(2-ethynylphenyl)-ethynyl benzal-

dehyde molecules, and the oxygen atoms of Cu–O chains have a good activity to oxidize both the alkynyl and the aldehyde groups and thus activate the molecules adsorbed at the interface. Moreover, the alkynyl group is more facile to be oxidized by the oxygen atoms of Cu–O than the aldehyde group because of the strong interaction between the alkynyl group and the interface. Besides demonstrating the role of the interface in catalytic reactions, our present findings may also have important implications for creating atomic-scale models to explain the mechanism of reactions occurring over oxide species supported on metal in real catalytic conditions. First, the oxygen atoms of oxide species could be abstracted by the adsorbed molecules, forming oxygen vacancies on oxide species, and then, the additional  $O_2$  will be dissociated at the oxygen vacancies and refill them to keep the catalytic activity. A similar mechanism has been proposed for the oxidation reactions occurring on  $CeO_2$ -containing catalysts.<sup>[1f,4]</sup>

## Experimental Section

The experiments were performed in a ultrahigh-vacuum chamber (base pressure  $2 \times 10^{-10}$  mbar) equipped with a SPECS variable-temperature STM.<sup>[5]</sup> The Cu–O chains were fabricated by using standard methods demonstrated previously.<sup>[6]</sup> The EBA molecules were loaded into a glass crucible that was mounted in a molecular evaporator. After the system was thoroughly degassed, the EBA molecules were deposited by thermal sublimation onto a Cu–O/Cu(110) substrate held at RT. The sample was thereafter transferred within the ultrahigh-vacuum chamber to the STM. All calculations were performed in the framework of DFT by using the Vienna ab initio simulation package (VASP).<sup>[7]</sup> The projector-augmented wave method was used to describe the interaction between ions and electrons.<sup>[8]</sup> The atomic structures were relaxed by using the conjugate gradient algorithm scheme as implemented in the VASP code until the forces on all unconstrained atoms were  $\leq 0.03$  eV  $\text{\AA}^{-1}$ .

## Acknowledgements

We acknowledge the financial supports from the National Natural Science Foundation of China (21103128 and 91023008), the Program for New Century Excellent Talents in University (NCET-09-0607), the Shanghai Pujiang Program (11J1409700), the Shanghai “Shu Guang” project supported by Shanghai Municipal Education Commission and Shanghai Education Development Foundation (11SG25), the Fundamental Research Funds for the Central Universities, and Shanghai Leading Academic Discipline Project (B502).

**Keywords:** adsorption • copper • density functional calculations • scanning probe microscopy • supported catalysts

- [1] a) J. B. Reitz, E. I. Solomon, *J. Am. Chem. Soc.* **1998**, *120*, 11467–11478; b) M. Schur, B. Bems, A. Dassenoy, I. Kassatkine, J. Urban, H. Wilmes, O. Hinrichsen, M. Muhler, R. Schlögl, *Angew. Chem.* **2003**, *115*, 3945–3947; *Angew. Chem. Int. Ed.* **2003**, *42*, 3815–3817; c) R. Becker, et al., *Angew. Chem.* **2004**, *116*, 2899–2903; *Angew. Chem. Int. Ed.* **2004**, *43*, 2839–2842; d) D. Gamarra, C. Belver, M. Fernández-García, A. Martínez-Arias, *J. Am. Chem. Soc.* **2007**, *129*, 12064–12065; e) J. A. Rodríguez, et al., *Angew. Chem.* **2009**, *121*, 8191–8194; *Angew. Chem. Int. Ed.* **2009**, *48*, 8047–

- 8050; f) F. Yang, J. Graciani, J. Evans, P. Liu, J. Hrbek, J. F. Sanz, J. A. Rodriguez, *J. Am. Chem. Soc.* **2011**, *133*, 3444–3451; g) M. Behrens, et al., *Science* **2012**, *336*, 893–897.
- [2] a) T. Schalow, et al., *Angew. Chem.* **2005**, *117*, 7773–7777; *Angew. Chem. Int. Ed.* **2005**, *44*, 7601–7605; b) Q. L. Tang, Q. J. Hong, Z. P. Liu, *J. Catal.* **2009**, *263*, 114–122; c) Q. Fu, et al., *Science* **2010**, *328*, 1141–1144; d) Y. Yamada, C. K. Tsung, W. Y. Huang, Z. Y. Huo, S. E. Habas, T. Soejima, C. E. Aliaga, G. A. Somorjai, P. D. Yang, *Nat. Chem.* **2011**, *3*, 372–376; e) P. C. Stair, *Nat. Chem.* **2011**, *3*, 345–346; f) J. Jung, H. J. Shin, Y. Kim, M. Kawai, *J. Am. Chem. Soc.* **2012**, *134*, 10554–10561.
- [3] a) T. J. Huang, D. H. Tsai, *Catal. Lett.* **2003**, *87*, 173–178; b) Y. Z. Feng, X. L. Zheng, *Nano Lett.* **2010**, *10*, 4762–4766; c) Q. H. Zhang, W. P. Deng, Y. Wang, *Chem. Commun.* **2011**, *47*, 9275–9292.
- [4] a) S. Park, J. M. Vohs, R. J. Gorte, *Nature* **2000**, *404*, 265–267; b) F. Esch, S. Fabris, L. Zhou, T. Montini, C. Africh, P. Fornasiero, G. Comelli, R. Rosei, *Science* **2005**, *309*, 752–755.
- [5] a) F. Besenbacher, *Rep. Prog. Phys.* **1996**, *59*, 1737–1802; b) E. Laegsgaard, L. Osterlund, P. Thstrup, P. B. Rasmussen, I. Stensgaard, F. Besenbacher, *Rev. Sci. Instrum.* **2001**, *72*, 3537–3542.
- [6] K. Kern, H. Niehus, A. Schatz, P. Zeppenfeld, J. Goerge, G. Comsa, *Phys. Rev. Lett.* **1991**, *67*, 855–858.
- [7] a) G. Kresse, J. Hafner, *Phys. Rev. B* **1993**, *48*, 13115–13118; b) G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169–11186.
- [8] a) P. E. Blöchl, *Phys. Rev. B* **1994**, *50*, 17953–17979; b) G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, *59*, 1758–1775.

---

Received: December 23, 2012

Published online on February 22, 2013