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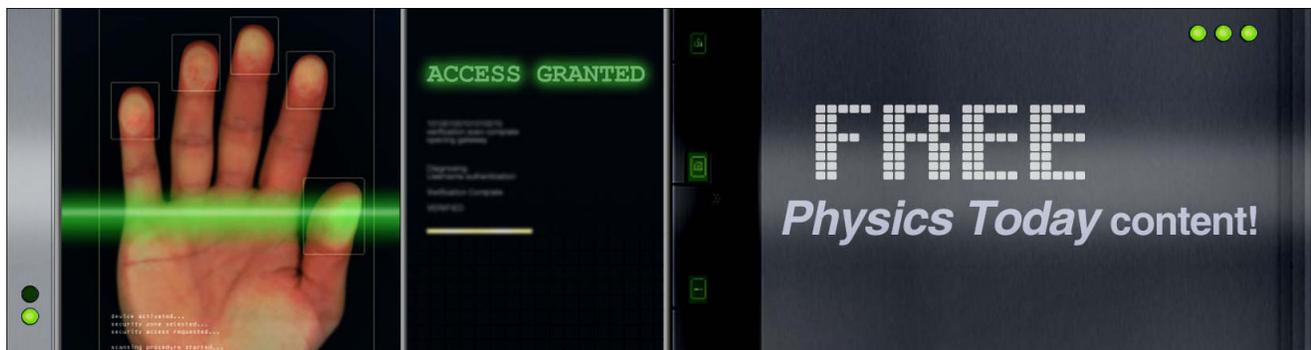
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## ADVERTISEMENT



## Controlling on-surface molecular diffusion behaviors by functionalizing the organic molecules with *tert*-butyl groups

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We have performed the systematic studies on three structurally similar aromatic molecules with different functional groups on a Cu(110) surface and investigated their on-surface molecular diffusion behaviors by the interplay of scanning tunneling microscopy imaging and density functional theory calculations. We have found that the *tert*-butyl groups could significantly affect the molecular adsorption geometries and moreover the mobility of the molecules on the surface. These findings could give further insights into the understanding of diffusion behaviors of organic molecules specifically with *tert*-butyl groups on surfaces. © 2013 AIP Publishing LLC.

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The dynamic behaviors of organic molecules on solid surfaces always play a vital role in surface physicochemical processes. Surface diffusion, as one of the preliminary dynamic behaviors of organic molecules for achieving more complex phenomena including film growth, heterogeneous catalysis, on-surface chemical reaction and the realization of nanodevices with advanced functions, has received a lot of attentions.<sup>1–7</sup> In general, by delicately controlling the molecular structures and choosing the appropriate substrates, different molecular diffusion behaviors could be regulated on surfaces. For example, the isotropic mobility could be turned into unidirectional motions by modifying the adsorbates with fullerene “wheels”<sup>6</sup> or two sequentially moving thiol substrate linkers;<sup>4</sup> later on, the fullerene molecules were shown to diffuse along the  $[1\bar{1}0]$  direction of Pd(110) surface resulting from the confinement of the substrate lattice.<sup>7</sup> Moreover, the *tert*-butyl groups were reported to be capable of regulating the diffusion behaviors of organic molecules by increasing the distance between surface and  $\pi$ -system of the molecules,<sup>8</sup> or controlling the registry between the molecules and the substrate.<sup>1</sup> Although previous studies have demonstrated some advancements in these aspects, it is, however, still of general interest to systematically study the influence of functional groups on the diffusion behaviors of organic molecules on surfaces, and to get further insights and deeper understanding on various dynamic behaviors occurring in a more complicated situation.

In this work, we focus on the influence of *tert*-butyl groups on the mobility of organic molecules on a Cu(110) surface.<sup>1,8</sup> We have designed three aromatic molecules,

(*Z*)-1,6-di(naphthalen-2-yl)hexa-3-en-1,5-diyne, tetrakis(phenylethynyl)ethane and (*Z*)-1,6-bis-(4-(*tert*-butyl)phenyl)hexa-3-en-1,5-diyne, shortened as DNHD, TPEE, and BtPHD, respectively (the structure models are shown in

Fig. 1). The TPEE molecule ( $C_{34}H_{20}$ ) and the BtPHD molecule ( $C_{26}H_{28}$ ) are both derived from the DNHD molecules ( $C_{26}H_{16}$ ). The TPEE has similar functional groups as DNHD but with larger molecular weight, and the BtPHD has similar molecular weight as DNHD but with different functional group (the *tert*-butyl-phenyl groups replacing the naphthyl groups). From an interplay of high-resolution ultra-high vacuum (UHV) scanning tunneling microscopy (STM) imaging and density functional theory (DFT) calculations, we have shown that both the DNHD and the TPEE molecules adopted planar adsorption geometries and exhibited high mobility on the Cu(110) surface, while the BtPHD molecule with terminal *tert*-butyl groups preferred a tilted geometry and, surprisingly, demonstrated distinctly low mobility comparing to that of the DNHD and TPEE molecules. These findings provide further insights into a complementary understanding on how the *tert*-butyl groups could influence the molecular adsorption behaviors and moreover the mobility of molecules on the surface, and also indicate that the *tert*-butyl groups could be good candidates for delicately controlling the dynamic behaviors of aromatic molecules on surfaces.

The STM experiments were performed in an UHV chamber (base pressure  $1 \times 10^{-10}$  mbar) equipped with a variable-temperature “Aarhus-type” STM purchased from SPECS.<sup>9,10</sup> The compounds were loaded into three separated glass crucibles in a molecular evaporator. After the system was thoroughly degassed, the compounds were deposited by thermal sublimation onto a Cu(110) substrate. The sample was thereafter transferred within the UHV chamber to the STM, where measurements were carried out at  $\sim 100$  K. All the calculations were carried out in the framework of DFT by using the Vienna *ab initio* simulation package (VASP).<sup>11,12</sup> The projector augmented wave method was used to describe the interaction between ions and electrons.<sup>13,14</sup> The atomic structures were relaxed using the conjugate gradient algorithm scheme as implemented in the VASP code until the forces on all unconstrained atoms were  $\leq 0.03$  eV/Å.

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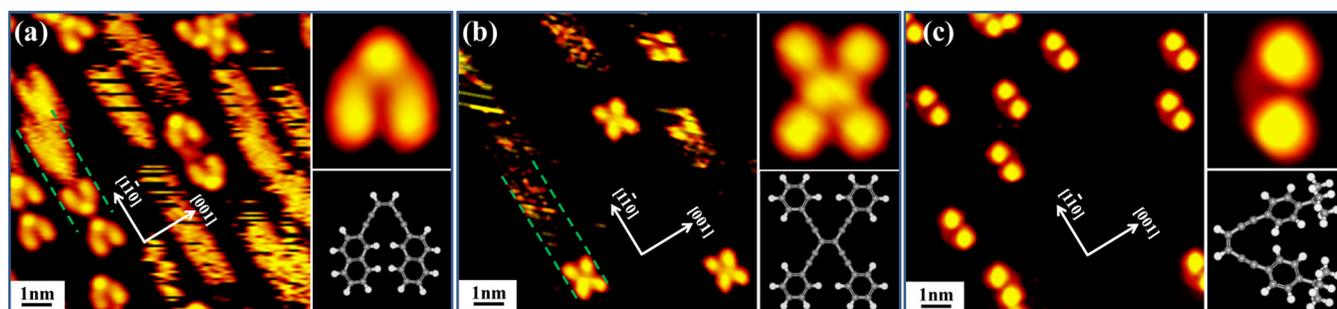


FIG. 1. STM images recorded with the same scanning parameter after depositing (a) DNHD, (b) TPEE, and (c) BtPHD on Cu(110). The close-up STM images and the gas-phase relaxed molecular models (H: white, C: gray) were shown in the upper-right and lower-right panels, respectively. Scanning condition:  $I_t = 0.7$  nA;  $V_t = -2500$  mV;  $T = 100$  K.

As shown in Fig. 1(a), after deposition of the DNHD molecules on Cu(110) at low temperature ( $\sim 170$  K) we found that the isolated molecules were distributed on the surface and appeared as heart shapes with two elliptical lobes and one round protrusion (cf. the close-up STM image), which suggested that the DNHD molecule adopted a flat-lying geometry on Cu(110). We assign the two elliptical lobes to the naphthyl groups and the round protrusion to the vinyl group as compared with the gas-phase relaxed molecular model. The DNHD molecules mainly adsorbed with the symmetry axis aligning along the  $[1\bar{1}0]$  direction of the substrate. Interestingly, during scanning we found that there were some blurred heart shapes in the large-scale STM images, and these blurred shapes were also mainly along the  $[1\bar{1}0]$  direction of the substrate and their widths were equal to that of the DNHD molecule as indicated by the parallel green lines in Fig. 1(a). It should be noted that the seemingly stationary molecules in Fig. 1(a) were also found to be mobile as reflected in the sequential STM images by keeping scanning on the same region (not shown). We could thus infer that the blurs are attributed to the trajectories of the mobile DNHD molecules diffusing along the  $[1\bar{1}0]$  direction resulting from the much higher mobility of the molecules on the surface comparing with the scanning speed (the typical time for recording one frame is about 10 s), which is a common phenomenon in STM experiments. Note that the molecular diffusion direction is unidirectional and different from the scanning direction (from left to right); thus, the tip-induced diffusion behavior could be excluded.

To investigate the influence of molecular weight on the molecular diffusion behaviors, we deposited the TPEE molecules (which could be roughly regarded as functionalizing the DNHD molecules with two more aromatic legs) on Cu(110) at  $\sim 170$  K and performed the STM experiments in the same conditions as for DNHD molecules. As shown in Fig. 1(b), similarly, the isolated TPEE molecules were distributed on the surface at a relatively low coverage and appeared as four peripheral lobes and one central protrusion (cf. the close-up STM image), and we assigned the four lobes to the phenyl groups and the center protrusion to the vinyl group as compared with the gas-phase relaxed molecular model. Just like the case of the DNHD molecules, the TPEE molecules preferred to lie flat on the Cu(110) surface with the long symmetry axis aligning along the  $[1\bar{1}0]$  direction of the substrate. Moreover, though two more aromatic “legs” have been added onto the TPEE molecule, there were still blurred trajectories

moving along the  $[1\bar{1}0]$  direction with the same width as the TPEE molecules as indicated by the parallel green lines in Fig. 1(b), which was the sign that the TPEE molecules were still highly mobile on the Cu(110) surface.

To further explore the influence of functional groups on the molecular diffusion behaviors, we deposited the BtPHD molecules (which replaced the naphthyl groups of the DNHD molecule by the *tert*-butyl-phenyl groups) on Cu(110) at  $\sim 170$  K and performed the STM experiments under the same conditions. As shown in Fig. 1(c), the isolated BtPHD molecules exhibited in STM images as two bright protrusions corresponding to high electron tunneling probability through the *tert*-butyl groups to the substrates.<sup>15–17</sup> Since the *tert*-butyl groups dominated the STM image of a single BtPHD molecule, the vinyl group of the molecule just appeared as dark protrusion (cf. the close-up STM image and the gas-phase relaxed molecular model). The BtPHD molecules also preferred to isolatedly distribute on Cu(110) at a relative low coverage, yet, mainly adsorbed with the symmetry axis aligning perpendicular to the  $[1\bar{1}0]$  direction. More interestingly, unlike the cases of the DNHD and TPEE molecules, there were no blurred trajectories observed during the scanning process, which was a sign of relatively low mobility of BtPHD molecules. From the experiment, it was obvious that the *tert*-butyl groups could significantly affect the adsorption

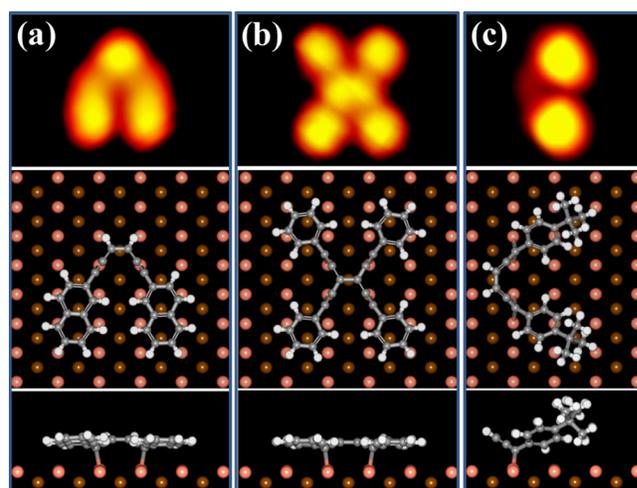


FIG. 2. The close-up STM images and DFT optimized adsorption geometries of (a) DNHD, (b) TPEE, and (c) BtPHD molecules on Cu(110). The middle panels are top-view models and the lower panels are side-view models.

geometry and the mobility of the BtPHD molecule on Cu(110).

DFT calculations have been performed to understand the adsorption geometries of three molecules on Cu(110) at atomic scale. The optimized models of DNHD, TPEE, and BtPHD molecules on the Cu(110) surface were depicted in Fig. 2. As seen from the models both the DNHD and the TPEE molecules prefer to adopt flat-lying configurations, which is well consistent with the STM results. While, the BtPHD molecule tends to adsorb with a non-planar configuration in which the carbon atoms adjacent to the phenyl groups are in close proximity to the substrate, while the vinyl and *tert*-butyl-phenyl groups are tilted upwards as clearly illustrated in the side view of the model (cf. Fig. 2(c)). The STM and DFT results are in good agreement and match well with the previous studies that organic molecules mainly constituted by the aromatic  $\pi$ -conjugated groups tend to adopt planar geometries on surfaces,<sup>18–20</sup> and the *tert*-butyl groups could influence the molecular adsorption geometries by lifting up the molecules from surfaces.<sup>8</sup>

To get further insights into the different diffusion behaviors of these three molecules on Cu(110), we have also calculated the potential energy profiles for the diffusions of three

molecules along the  $[1\bar{1}0]$  direction as illustrated in Fig. 3. In the calculations, several stable configurations along the  $[1\bar{1}0]$  direction between two adjacent most stable adsorption sites were calculated, and interpreted as intermediate states for the molecular diffusions.<sup>15,21</sup> The DNHD and TPEE molecules have very close diffusion barriers determined to be 0.195 eV and 0.175 eV, respectively, while the BtPHD molecule has a larger barrier of 0.325 eV. We can also estimate the rate constant of three molecules in the experimental condition ( $\sim 100$  K) based on the Arrhenius equation<sup>4,22</sup>

$$k = Ae^{-E_a/RT}. \quad (1)$$

By supposing a typical prefactor  $A$  of  $10^{13} \text{ s}^{-1}$ , we obtain an estimated rate constant of  $1.49 \times 10^3 \text{ s}^{-1}$  for DNHD,  $1.51 \times 10^4 \text{ s}^{-1}$  for TPEE, and  $4.17 \times 10^{-4} \text{ s}^{-1}$  for BtPHD. The difference of nearly 8 orders of magnitude between the mobile and the immobile molecules indicates that at  $\sim 100$  K the DNHD and TPEE molecules could be highly mobile while BtPHD remains motionless, which is in excellent agreement with the STM findings.

From the STM experiments and DFT calculations, it is clearly seen that the mobility of the DNHD molecule could

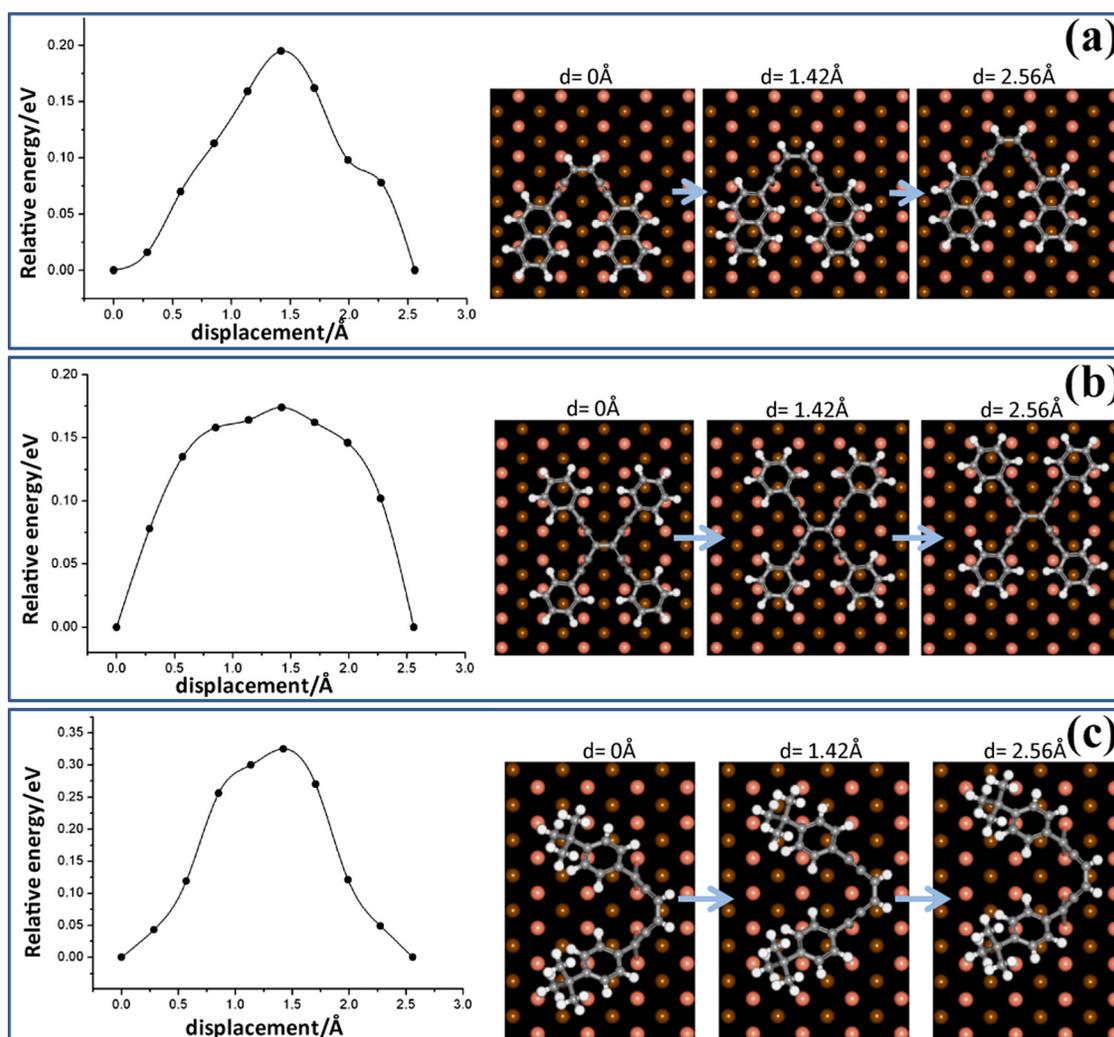


FIG. 3. The potential energy profiles for the diffusion of (a) DNHD, (b) TPEE, and (c) BtPHD molecules on Cu(110) as a function of the displacement along the  $[1\bar{1}0]$  direction. The two zero points of the relative energy curves (at  $d = 0 \text{ \AA}$  and  $d = 2.56 \text{ \AA}$ ) correspond to the two adjacent most stable sites separated by the lattice constant of Cu(110) along the  $[1\bar{1}0]$  direction. The maxima of the relative energy curves (at  $d = 1.42 \text{ \AA}$ ) correspond to the transition states.

be significantly changed by functionalizing with the *tert*-butyl groups. Two possible points can be singled out with respect to the decreased mobility of the BtPHD molecule on Cu(110): (1) the *tert*-butyl groups are in a specific registry with Cu(110) to lock the molecule on the surface<sup>1</sup> and (2) the tilted molecular adsorption geometry caused by the *tert*-butyl groups inhibits the surface diffusion behavior since the flat-lying TPEE molecule (with larger molecular weight) could freely diffuse on the surface. Note that the case for the BtPHD is different from the one showing that the mobility of aromatic molecules could be increased when lifting the whole molecule away from the substrate by functionalizing with *tert*-butyl groups.<sup>8</sup> In our case, only one side of the BtPHD molecule was lifted resulting in a seesaw-like situation. This study has thus given us a complementary understanding on the influence of the *tert*-butyl groups on the diffusion behaviors of aromatic molecules on surfaces.

In conclusion, by combining the high-resolution UHV-STM imaging and DFT calculations, we have systematically investigated the adsorption and diffusion behaviors of three aromatic molecules on Cu(110) at the atomic scale. These results reveal that the *tert*-butyl groups could greatly influence the adsorption geometries and mobility of aromatic molecules on the surface, and thus could be one of the good candidates as functional group to control the molecular dynamic behaviors on surfaces. Further works could be explored to generalize the application of the *tert*-butyl group as a modulator on other molecular systems to get a deeper understanding on the influence of the *tert*-butyl groups in more sophisticated situations.

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- <sup>1</sup>R. Otero, F. Hummelink, F. Sato, S. B. Legoas, P. Thostrup, E. Laegsgaard, I. Stensgaard, D. S. Galvao, and F. Besenbacher, *Nature Mater.* **3**, 779 (2004).
- <sup>2</sup>T. Mitsui, M. K. Rose, E. Fomin, D. F. Ogletree, and M. Salmeron, *Science* **297**, 1850 (2002).
- <sup>3</sup>K. L. Wong, G. Pawin, K. Y. Kwon, X. Lin, T. Jiao, U. Solanki, R. H. J. Fawcett, L. Bartels, S. Stolbov, and T. S. Rahman, *Science* **315**, 1391 (2007).
- <sup>4</sup>K. Y. Kwon, K. L. Wong, G. Pawin, L. Bartels, S. Stolbov, and T. S. Rahman, *Phys. Rev. Lett.* **95**, 166101 (2005).
- <sup>5</sup>L. Gross, F. Moresco, M. Alemani, H. Tang, A. Gorudon, C. Joachim, and K. H. Rieder, *Chem. Phys. Lett.* **371**, 750 (2003).
- <sup>6</sup>Y. Shirai, A. J. Osgood, Y. Zhao, K. F. Kelly, and J. M. Tour, *Nano Lett.* **5**, 2330 (2005).
- <sup>7</sup>J. Weckesser, J. V. Barth, and K. Kern, *Phys. Rev. B* **64**, 161403 (2001).
- <sup>8</sup>M. Schunack, T. R. Linderoth, F. Rosei, E. Laegsgaard, I. Stensgaard, and F. Besenbacher, *Phys. Rev. Lett.* **88**, 156102 (2002).
- <sup>9</sup>F. Besenbacher, *Rep. Prog. Phys.* **59**, 1737 (1996).
- <sup>10</sup>E. Laegsgaard, L. Österlund, P. Thostrup, P. B. Rasmussen, I. Stensgaard, and F. Besenbacher, *Rev. Sci. Instrum.* **72**, 3537 (2001).
- <sup>11</sup>G. Kresse and J. Hafner, *Phys. Rev. B* **48**, 13115 (1993).
- <sup>12</sup>G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- <sup>13</sup>P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- <sup>14</sup>G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- <sup>15</sup>J. K. Gimzewski, C. Joachim, R. R. Schlittler, V. Langlais, H. Tang, and I. Johansson, *Science* **281**, 531 (1998).
- <sup>16</sup>N. Wintjes, D. Bonifazi, F. Cheng, A. Kiebele, M. Stohr, T. Jung, H. Spillman, and F. Diederich, *Angew. Chem., Int. Ed.* **46**, 4089 (2007).
- <sup>17</sup>M. Schunack, L. Petersen, A. Kuhnle, E. Laegsgaard, I. Stensgaard, I. Johansson, and F. Besenbacher, *Phys. Rev. Lett.* **86**, 456 (2001).
- <sup>18</sup>M. Parschau, R. Fasel, K. H. Ernst, O. Groning, L. Brandenberger, R. Schillinger, T. Greber, A. P. Seitsonen, Y. T. Wu, and J. S. Sieger, *Angew. Chem., Int. Ed.* **46**, 8258 (2007).
- <sup>19</sup>J. Schnadt, W. Xu, R. T. Vang, J. Knudsen, Z. Li, E. Laegsgaard, and F. Besenbacher, *Nano Res.* **3**, 459 (2010).
- <sup>20</sup>J. Schnadt, E. Rauls, W. Xu, R. T. Vang, J. Knudsen, E. Laegsgaard, Z. Li, B. Hammer, and F. Besenbacher, *Phys. Rev. Lett.* **100**, 046103 (2008).
- <sup>21</sup>D. Jiang and S. Dai, *J. Phys. Chem. C* **113**, 3763 (2009).
- <sup>22</sup>D. Jiang and S. Dai, *Phys. Chem. Chem. Phys.* **11**, 8601 (2009).