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Using X-ray Photoelectron Spectroscopy we observe breaking of the strong interatomic bond in molecular CO at low temperature on a stepped Cu surface. Since the electronic structure of Cu does not allow for the splitting of CO at such low temperatures it suggests that there may be a less obvious pathway for the process. Through X-ray Photoelectron Spectroscopy we can clearly identify products associated with the dissociation of CO and the subsequent formation of stable graphitic carbon on the surface. However the dissociation of CO can be inhibited when the stepped Cu surface is kept clean from surface carbon. These observations imply that the reaction is driven by the presence of small amounts of weakly bound carbon at the surface. DFT calculations confirm that carbon atoms on a stepped Cu surface indeed are the preferred adsorption sites for CO, which increases the stabilization of CO on the surface and weakens the C-O bond. This results in the breaking of the C-O bond at the step edge via the Boudouard reaction ($2CO_{ads} \rightarrow C_{ads} + CO_2$) with a barrier of 0.71 eV.

The splitting of the internal C-O bond in carbon monoxide is essential as a fundamental step for various catalytic fuel synthesis processes [1,2] such as methanation, methanol synthesis, Fischer-Tropsch synthesis and electrocatalytic conversion of CO_2 to hydrocarbons [3]. CO dissociation plays a crucial role for C-C coupling towards the formation of higher hydrocarbons and alcohols. An optimal catalyst must be able to reduce the activation energy for breaking the strong CO triple bond in CO. Meanwhile the catalyst has to bind the reaction products sufficiently without poisoning the surface. Usually the catalytic trend of metals shows that these aspects are counteractive resulting in a volcano-type relationship for optimum activity and bond strength. [4] The coinage metals (Cu, Ag and Au) binds carbon weakly, which allows the adsorbed carbon fragments to easily diffuse and re-combine on the surface. The important C-C coupling processes at low temperature [5,6] could become feasible, which may open an avenue for new and exciting processes on surfaces. However, the barrier for CO dissociation on coinage metals is too high. [4] If some additions of other elements on the surface could stimulate a dissociation process of CO at low temperatures it could favorably enable coinage metals to become a C-C coupling catalyst.

Here we report on an alternative route to dissociate CO on a coinage metal. We show a direct experimental evidence of CO dissociation assisted by minor amounts of carbon at a surprisingly low temperature on a stepped Cu surface. We propose that this is a result of CO interacting with carbon atoms close to undercoordinated sites on the Cu surface. We combine results from X-ray Photoelectron Spectroscopy (XPS) at temperatures from 110 K to room temperature and Density Functional Theory (DFT) calculations to study CO dissociation on stepped (211) and close-packed (111) Cu surfaces. From the XPS spectra, we see evidence of the conversion of CO into first surface carbon and subsequently graphene. From DFT calculations we show that an alternative low

barrier pathway for CO to dissociate exists at the step edge of Cu in the presence of carbon.

The XPS experiments were performed at the Surface Science Endstation (SSE) respective the APXPS (Ambient Pressure XPS) Endstation [7] at beamline 13-2, Stanford Synchrotron Radiation Lightsource (SSRL), California, USA. The Cu(211) and Cu(111) single-crystals were cleaned by many cycles of Ne$^+$ sputtering at 1 kV and annealing to 950K in the preparation chamber of the endstations. CO was passed through a hot (520 K) Cu-based scrubber before it was leaked with a precision leak valve into the XPS chamber. As checked with XPS, this effectively scrubbed away nickel carbonyl that could contaminate the Cu surfaces. The cleanliness of the surface was checked with XPS. CO was leaked directly into the analysis chambers of both endstations while the beamline shutter was blocking the x-ray beam. This ensured that the observed effects were not beam induced. The UHV experiments at SSE were conducted at low temperature (110 K) while the APXPS experiments at room temperature. Ab initio calculations were performed with the Quantum Espresso code [8] using a plane-wave basis set in the generalized gradient approximation with the BEEF-vdW exchange-correlation functional, which explicitly takes long-range dispersion forces into account [9]. A 500 eV wave function cutoff and 5000 eV density cutoff were employed. Stepped surfaces were modeled using a 12 layer (3 x 1) unit cell resulting in a slab with 4 layers in the (111) direction having monoatomic steps of 3 atoms wide with a (100) geometry. More than 12 Å of vacuum was included to separate periodic images and the Brillouin zone was sampled using a (4 x 4 x 1) Monkhorst-Pack grid [10]. In all calculations the adsorbates and the Cu atoms in the two topmost (111) layers were allowed to relax until the forces became smaller than 0.05 eV/Å. For all the transition state structures we found a single imaginary frequency thus identifying the geometry as a first-order saddle-point on the potential energy curve. The vibrational frequencies were calculated within the harmonic approximation.

Figure 1 shows the XPS C and O1s spectra for the stepped Cu(211) at 110 K (a), after dosing 3L of CO on Cu (b) and after annealing CO/Cu to 150 K (c). The initial Cu surface has 2% of graphitic carbon relative to the total amount adsorbed molecular CO. CO coverage on Cu(211) after exposure to 3L of CO at 110 K is approximated to be between 1/6 and 1/2 ML. The estimation is derived from Refs [11-13], where CO adsorbs in (2x1) at on-top site of Cu atoms at the step edges. The adsorption of molecular CO results in a structurally rich C 1s spectrum (b), where peak Cu-CO (blue) represents the main peak for adsorbed molecular CO and S1 (green) and S2 (orange) are the shake-up structures, as explained by Tillborg et al [14]. Peak G (black) is the graphitic carbon that is mostly inherited from the Cu surface in (a) although peak G is now more symmetric and narrower. Upon annealing to 150 K (c) some molecular CO desorbs from the surface. Meanwhile a new peak C' (magenta) appears in the lower binding energy side (282.6 eV) and the intensity of peak G at 284.3 eV has increased. This implies a conversion of molecular CO into carbon products represented by peak C' and G on the stepped Cu surface. Peak G is assigned to graphene on Cu, in accordance to [15]. Due to the very low binding energy of peak C' we relate it to carbidic-like surface carbon. Such a low binding energy assigned to gold carbide has been observed previously. [16,17] The total amount of C' and G has increased to 6.3% indicating CO dissociation.

The fact that carbidic species is not observed after measuring the CO on Cu(211) sample at 110 K [Fig. 1(b)] is a strong evidence that CO dissociation is not beam induced. We have also measured the sample after annealing to 150 K [similar to Fig. 1(c)] repeatedly on the same spot for over 20 min and still we do not observe change in neither spectral shape nor peak relative intensity. In addition we have dosed CO below the desorption temperature and subsequently annealing the sample to stimulate desorption

without exposing to the beam. Yet we still observe similar peak G and C' to Fig. 1(c) in the C 1s spectra measured post-annealing.
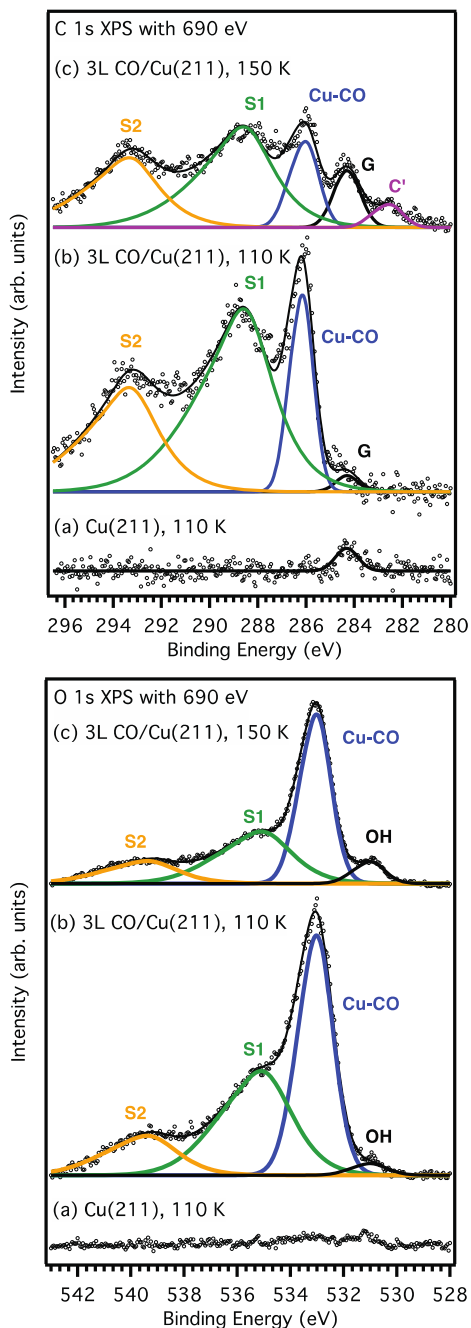

FIG. 1 (color online). [Top] C 1s and [Bottom] O 1s XPS spectra recorded from (a) a Cu(211) surface at 110 K, (b) 3L of CO/Cu(211) at 110 K and (c) after annealing the CO/Cu(211) system to 150 K. All spectra were acquired by setting the photon energy to 690 eV.

(Spectra not shown here) These observations show that the reported CO dissociation is not related to beam exposure.

The corresponding O 1s spectra show only a small change, i.e. CO desorption upon annealing. The small feature at 531.0 eV can be related to dissociated products with a binding energy close to OH. It amounts to only 1.5% of the total molecular CO coverage and most likely appears through reactions with small amount of dissociated water on the surface. It is known that water dissociates on Cu(110), as shown in [18,19]. The amount of oxygen species due to CO dissociation is much less than carbon indicating that oxygen is removed from the surface, most likely as CO_2. Clearly there is a dissociative event occurring on the surface between 110 and 150 K.

We evaluated the role of steps by comparing the reactivity of a stepped Cu(211) surface with a flat Cu(111) surface. Since (111) is in general an inert surface we used higher CO exposures utilizing APXPS. The C 1s spectra (Supplemental material Fig. S1) [20] clearly show a profound difference on the surface adsorbates between the stepped and the flat Cu surface consequent to a substantial CO exposure at 10 Torr for 10 min at room temperature. The Cu(211) surface is dominated by graphitic and carbidic carbon while the flat surface remains almost clean. This signifies that the CO adsorption sites on Cu(211) are different from on Cu(111).

To understand the chemical nature of these C 1s peaks we performed DFT calculations for different CO reaction scenarios on flat Cu(111) and stepped Cu(211) surfaces, as shown in Fig. 2. Our results in Fig. 2(a) show that the barriers for direct dissociation on Cu(111) and Cu(211) is 4.50 eV and 4.12 eV respectively, which is extremely high. This indicates that the observed formation of surface carbon and graphene cannot be the result of CO dissociation on the pure Cu surfaces even in the presence of step sites. The question is what mechanism allows dissociation to occur at the surface step sites but not on the terrace sites, which we observed in the XPS results. Our hypothesis is that a reactive carbon

species exist on the stepped surface, which can facilitate another reaction pathway.

In fact we find that CO binds with 2.20 eV and 1.67 eV to a carbon monomer (C1) and dimer (C2) on the Cu(211) surface, respectively. This is 1.53 eV and 1.00 eV more stable than the most stable adsorption site for CO on the pure Cu(211), hence there is a strong driving force for forming
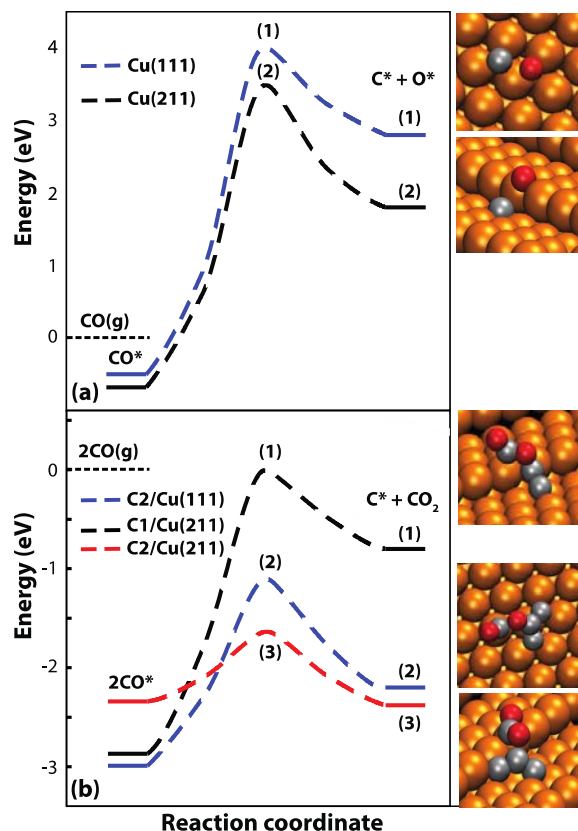

FIG. 2 (color online). Calculated barriers for the splitting of CO relative to a CO molecule in the gas phase a; on (1) a clean Cu(111) and (2) a Cu(211) model surface and b; on (1) a Cu(211) via CCO intermediate, (2) a Cu(111) via C2-CO intermediate and (3) a Cu(211) via C2-CO intermediate. Schematic insets show the transition state for each reaction. Color coding: orange for Cu, gray for C and red for oxygen.

such surface species. Whether surface carbon can be formed from CO depends strongly on the stabilization of the final product. This is resolved by incorporating the carbon in the graphene-like nucleus whereas the atomic oxygen produced from the CO bond breaking is consumed through a reaction with adjacent co-adsorbed CO on the

step site via a Boudouard type mechanism ($2CO_{ads} \rightarrow C_{ads} + CO_2$).

This is seen directly from the calculated barriers of 2.88 eV and 0.71 eV for breaking the C-O bond in C1-CO and C2-CO, respectively. See Fig. 2(b). The reason for this difference between the CO on a carbon monomer respective on a carbon dimer is that the final state for the monomer still requires that a bond between the carbon from CO and the Cu surface be formed. On the contrary for the dimer no bond between the carbon and the Cu surface is necessary. A barrier of 0.71 eV for the carbon dimer assisted reaction indicates that seeding of the graphene nucleation centers is possible and that further growth can be generated from CO even at relatively low temperatures. This will eventually lead to the formation of graphene islands. One of the essential factors for accessing this reaction channel is that the surface carbon is more reactive than the Cu surface itself. Consequently this limits the choice of elemental transition metals for such reaction to only the coinage metals.

To test the impact of Cu surface structure on the proposed CO dissociation mechanism we have performed the C2-CO calculation on the flat Cu(111) surface as well. We conclude that the process cannot proceed on the close-packed surface because the carbon trimer (C3) product is greatly destabilized on the Cu(111) surface as compared to the Cu(211) step. The limiting factor on the terrace is thus associated with a too high barrier of 1.70 eV (see Fig. 3). It has also been shown in calculations that the formation of carbide on flat Cu surface is not possible [21]. This is in perfect agreement with experiments as shown in Fig. S1(b) [20] where there is neither adsorbed CO nor significant changes in the C 1s signal is observed on the Cu(111) surface after CO is introduced.

To further strengthen our hypothesis on the necessity of surface carbon, we have exposed a thoroughly cleaned Cu(211), as evidenced by the XPS survey spectrum (Supplemental material Fig. S2, red spectrum [20]), to 10 Torr of CO for 10 min at room temperature. The absence of C 1s

signal (Supplemental material Fig. S2, inset [20]) from the Cu surface after the CO exposure clearly supports our claim that the presence of surface carbon on the steps is necessary for CO dissociation.
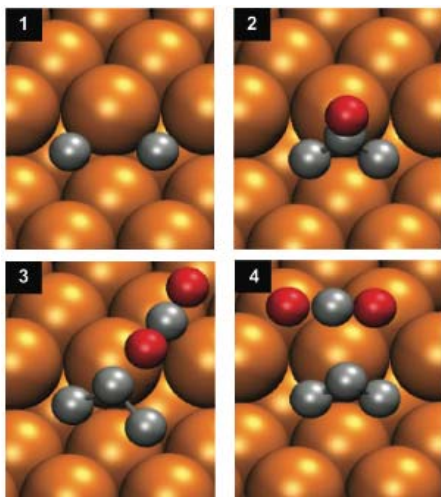

FIG. 3 (color online). Schematics for a suggested mechanistic model of CO dissociation on a Cu step edge decorated with surface carbon. The process propagates from Step 1 to Step 4. Color coding: orange for Cu, gray for C and red for oxygen.

Both our experimental observations and DFT calculations show strong evidence that surface carbon on stepped Cu can induce the dissociation of CO at temperatures as low as 150 K. The carbon components formed from this CO dissociation process can propagate rapidly into forming more stable graphitic structures. Therefore the observed dissociation products are a mixture of carbide-like carbons and graphene at low temperature and predominantly graphite-like at higher temperatures. Based on our results, we propose the CO adsorption and dissociation mechanistic model, as illustrated in Fig. 3. We consider two surface carbon atoms (C2) at the lower step edge of Cu (Fig. 3, Step 1). CO adsorbs on the carbon atoms and it results in a C2-CO bond formation (Fig. 3, Step 2) because the carbon dimer is an energetically favorable adsorption site. More incoming CO will adsorb on Cu atoms at the upper step edge and diffuse to sites adjacent to the C2-CO species, where the C-O bond of C2-CO is stretched (Fig. 3, Step 3). The disproportion of CO proceeds via the Boudouard reaction (Fig 3, Step 4) resulting in a graphene-like nucleus on the lower step edge and a molecular CO_2. When continuous CO dissociation proceeds through a similar sequence, the nucleus grows in size and gradually it forms a graphene island.

The fact that CO can dissociate at low temperature can be of importance for many processes involving carbon growth that is benefitial for making graphene-based electronic devices. Experimental evidences [22-25] show that high temperatures are needed to form the carbon components responsible for the nucleation of graphene. A graphene growth process operating below room temperature reduces problems associated with the dynamics of the metal template. Another important area is the effort to reduce CO_2 from the atmosphere and thus limiting carbon emissions. It has been shown that Cu electrodes can be employed for electrochemical CO_2 reduction for producing hydrocarbons and alcohols at reasonable overpotentials [2,3,26] and there are recent intriguing results indicating that nanostructured Cu leads to lower overpotential with higher selectivity [27,28]. It is an open question if the current results here on a low-barrier carbon induced CO dissociation on step sites on Cu may play a role in the C-C coupling that is compulsory for forming ethylene and ethanol on nanostructured Cu [27,28].

In summary our experimental and theoretical results are in unison with the postulation that CO dissociation occurs via the adsorption of CO on highly reactive surface carbons at the inner step edge of Cu. The DFT calculations show that the bond activation barrier is significantly reduced when this CO reacts through the Boudouard reaction with an adjacent CO on the upper step edge of Cu. This causes the weakening and subsequently breaking of the C-O bond on the Cu step. The carbon from dissociated CO remains on the step and it initiates the nucleation of graphene. The observed carbon induced splitting of CO on

Cu may inspire new prospect of designing highly efficient and selective catalysts for fuel synthesis, and for a controlled growth of carbon nanotubes of a specific chirality for nano electronic devices.

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[20] See Supplemental Material at [*URL will be inserted by publisher*] for additional data.

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