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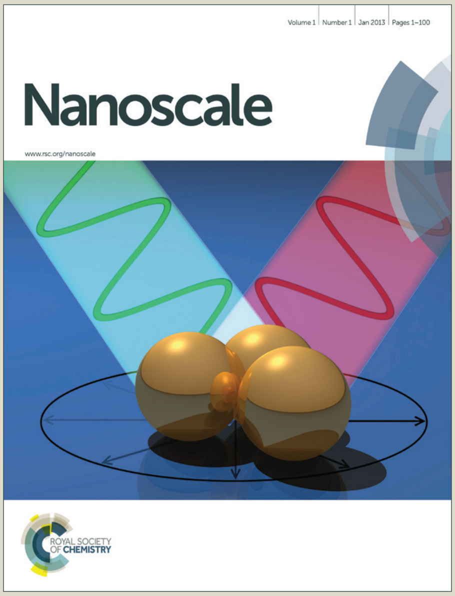

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Formation of Carbyne and Graphyne on Transition Metal Surfaces

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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The electronic and geometric structure of carbyne on various transition metal surfaces were investigated by theoretical calculations. It was found that carbyne on non-active metal surfaces has a polyynic structure, while a polycumulenic structure is more stable on active catalyst surfaces. The self-assembly of carbyne on metal substrate could lead to the synthesis of graphyne.

In nature, carbon atoms mostly exists as two forms -- being sp^3-hybridized, such as those in diamond, and being sp^2-hybridized, such as those in graphite, fullerene, carbon nanotubes or graphene. Another form of carbon is the sp^1-hybridized carbyne, which was proposed by a Russian scientists at about 50 years ago.[1] Each carbon atom in a carbyne is linked with two neighbors by alternative single/triple bonds in the form of "... ≡ C–C ≡ C–..." (named polyyne, Fig. 1a) or double bonds as "...=C=C=..." (named polycumulene, Fig. 1b).[2, 3] Carbyne is expected to have many interesting properties due to its unique linear structure. For example, the carbyne was predicated to be stronger than carbon nanotubes and graphene, probably the strongest known materials ever synthesized.[4-6] And carbyne was also expected to be the room temperature superconductor.[2] However, in contrast to the extensive study of other carbon materials, such as fullerene, carbon nanotube and graphene, the progresses and efforts on carbyne synthesis are still very limited. Such slow progress was mainly attributed to difficulties in stabilizing such one-dimensional structure. Early in 1950s, Pitzer et. al. predicted the possibility of synthesizing carbyne from a theoretical view point.[7] The prediction didn't draw much attention until Goresy and Donnay found a new allotrope of carbon named “chaoite” or ‘‘white carbon’’ in 1968.[8] Following the discovery of fullerenes, linear carbon chains alone or as parts of carbon nanostructures are widely observed in carbon-rich vapor.[9, 10] The carbyne was also found to exist in interstellar dust[11] and meteorites.[12] However, carbyne in nature is very limited and hard to be observed or extracted. In laboratory, carbyne can be prepared by gas-phase deposition,[13] electrochemical synthesis,[14] dehydrohalogenation of polymers[15] or other materials[10]. In all cases, the final products or materials are ill-defined, and as a consequence, most rich and unique properties of carbyne are unmeasured in experiments. So, finding proper method to synthesize stable carbyne is pressing and crucially important for both fundamental researches and applications.

Recently, during the study of graphene CVD growth on transition metal surfaces, e.g., Cu(111) and Ni(1111) surfaces, the exceptional stability of carbon chains up to N ~ 10 has been shown theoretically.[16-21] These theoretical results indicate a possibility of observing and measuring carbyne on metal surface directly. As is well-known, the carbon chains in vacuum are hard to be detected or measured because of their short life time and the low population.[22] While, the carbyne can be stabilized on a metal surface because the passivation and support from the metal substrate ensures a longer life-time and large population of carbyne, which makes the experimental detection and measurements on their properties become possible.

In this letter, we systematically investigated the formation of carbyne on four different metal surfaces, e.g. Cu(111), Ni(111), Rh(111) and Ru(0001). Our study shows that, depending on the activity of the metal surface, there are two types of carbyne formation, polyynic carbyne and polycumulenic carbyne. On active metal surfaces (e.g., Ru or Ru), the carbon chain has the polycumulenic structure. While, on less active metal surfaces (e.g., Cu(111)), long polyynic carbyne is more stable. These carbynes could maintain as the ground state until the size of about 10 carbon atom. Beyond the critical size, the sp^2 carbon network becomes more stable than the carbyne. Based on the stability of the carbyne, the potential of synthesizing random graphyne through the self-assembly of carbynes on catalyst surface is discussed.

The ground structure of carbyne has been an interesting and controversial topic in history. Higgens and Hoffman proposed that the polyynic carbyne (Fig. 1a, c) is more stable than the polycumulenic carbyne (Fig. 1b, d) based on the Huckel molecular orbital calculations.[23] However, other scientists such as Pitzer, Popov and Shustorovich hold different perspectives.[7] It is interesting that our study showed that the ground state of carbyne on a metal surface is highly dependent on the activeness of the metal surface. As shown in Fig. 1g and h, carbyne with 8 carbon atoms on a Cu(111) surface adopts the polyynic formation, while on a Ru(0001) surface, it is in a polycumulenic formation. Electron density analysis demonstrates that the polyynic structure on Cu(111) has very similar electron density population to that of the polyynic carbyne in vacuum, with alternative high and low electron densities on C-C bonds. The electron density of polycumulenic formation on Ru(0001) is similar to that of the polycumulenic carbyne, with uniformly distributed electron densities on each C-C bond.

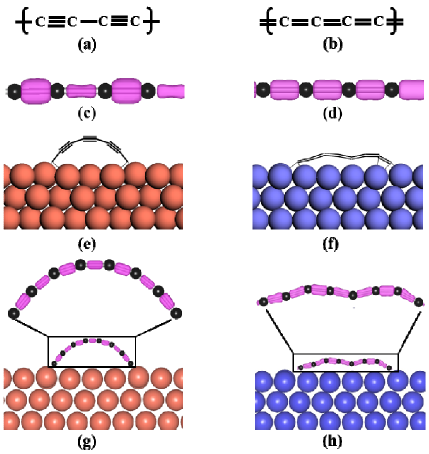

Fig. 1 The polyynic carbyne formation with alternative single and triple bonds (–C≡C–)n (a) and the polycumulenic carbyne with double bonding (=C=C=)n (b); the electron densities of polyynic carbyne (c) and polycumulenic carbyne (d); The formation of a carbon chain with 8 carbon atoms on Cu(111) surface (e) and Ru(0001) (f) surfaces and their corresponding electron densities (g, h).

Besides the electronic structure, the geometrical characteristics of carbyne on metal surfaces also depends on the activeness of the catalyst surface. The optimized carbyne on a Cu(111) surface is shown in Fig. 2a. It can be seen that each chain end is bound in the hollow site of the Cu(111) surface and the carbyne is in an arch shape. The formation of such a carbon arch can be regarded as a result of competition between the curvature energy of the arch and the passivation energy of the chain end. Similar to that of a graphene egde,[24, 25] the dangling bond on the end of a carbon chain can be more effectively passivated by standing on a metal surface. As shown in Fig. 2b, the larger the tilting angle, the lower the formation energy. For a carbon chain with both ends binding to the metal surface, such a tendency leads to the formation of bended carbyne arc. As shown in Fig. 2b, the tilt angle for C7 and C10 are 30 and 35 degree, respectively. Such tilting angles reduce the total formation energy of both ends by more than 2.0 eV than a straight carbyne laying on the surface.

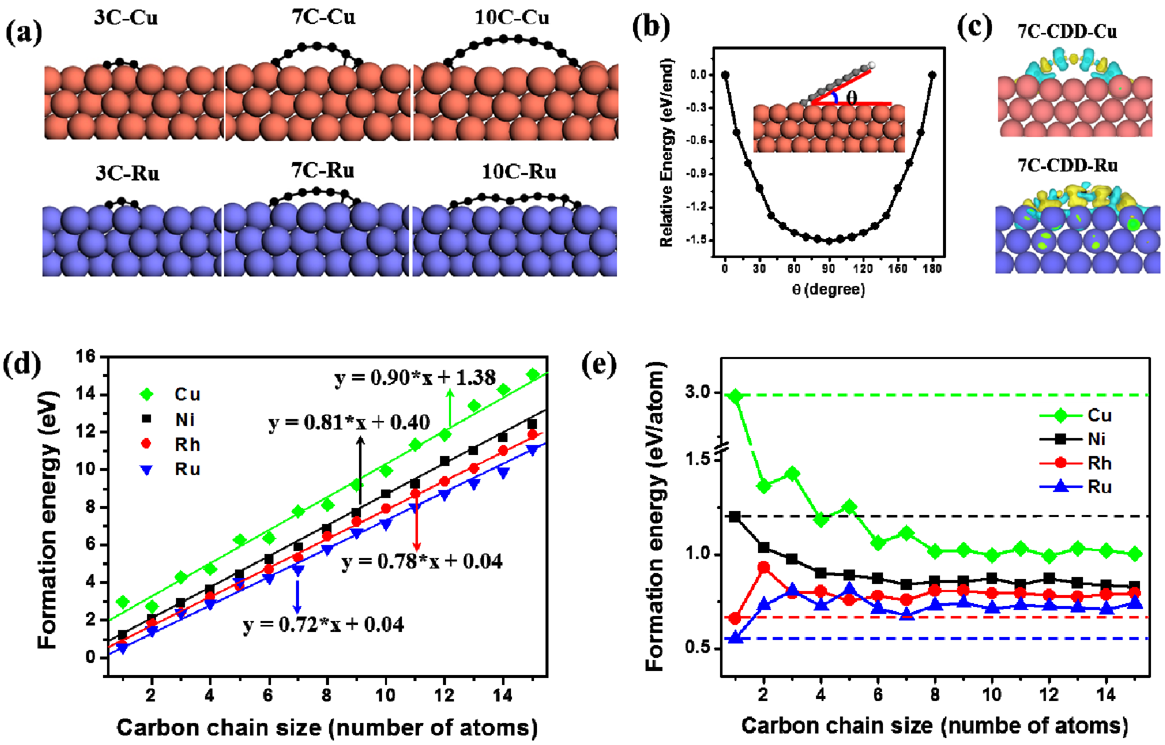

Fig. 2 (a) Selected structures of carbon chains (C3, C7, C13) on Cu(111) and Ru(0001) surfaces. (b) The relative binding energy of a carbyne on the Cu(111) surface as a function of the tilt angle, θ. (c) Charge density difference (CDD) for carbon chain with seven carbon atoms on Cu(111) and Ru(0001) surfaces. (d) Formation energies of carbyne/carbon chains (1C-15C) on Cu, Rh, Ru and Ni surfaces, respectively. And all the energies are fitted by the inserted linear equations. (e) Formation energies per carbon atom of carbon chains on Cu, Rh, Ru and Ni surfaces.

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In sharp contrast, the carbyne of various sizes on Ru(0001) surface are nearly parallel to the metal surface or just been slightly curved, as shown in Fig. 2a. Such difference can be attributed to the stronger interaction between the carbyne body and the metal surface due to the high activity of the Ru(0001) surface. Owing to the weak interaction between Cu(111) surface and carbon atom,[25, 26] only the end C atoms with dangling bonds interact strongly with the Cu surface (~ 3.1 eV per end atom). Those sp^1 hybridized C atoms in the body of the carbyne have very weak interaction with the substrate and thus can't hold the carbyne on the surface. While, for a carbon chain on Ru(0001) surface, the attraction between the body atoms of the carbyne and the metal surface becomes much stronger, as a consequence, the carbyne was stuck to the metal surface. The different interactions between the the carbyne and metal substrates can be clearly seen from the calculated charge density difference (CDD). As shown in Fig. 2c, the carbon chain on Ru(0001) surface has large amount of charge transfer from the metal substrate to the whole chain. Differently, there's nearly no visible charge transfer from the Cu(111) surface to the middle of carbyne. Further calculations showed that structures of carbyne on Ni(111) and Rh(111) surfaces are similar to that on Ru(0001) (details are presented in Figure S1 of supplementary information).

The formation energies of carbyne (from C1 to C15) on four different metal surfaces are plotted in Fig. 2d, where the energy of free-standing graphene is used as the reference. It can be seen the formation energy of the 1D carbyne increases linearly with size N, and thus these data can be fitted as:

$$E_{Car@M} = N \times E_{sp1} + 2 \times E_{end} \qquad (1)$$

where the energy increment of E_{sp1} can be interpreted as the energy difference between a C atom in the carbyne and that of in graphene, E_{end} is the formation energy of a metal passivated chain end, and N is the number of carbon atoms in the carbyne. From Fig. 2d we can see that both E_{sp1} and E_{end} depend on the type of metal surface, indicating the different binding strength of carbyne on metal substrate.

On Cu(111) surface, the E_{sp1} is as higher as 0.91 eV/atom, which means that a sp^1 hybridized carbon on Cu(111) surface is about 0.91 eV less stable than a carbon in graphene. For Ni(111), Rh(111) and Ru(0001) surfaces, the E_{sp1} are reduced to 0.81, 0.78 and 0.72 eV/atom respectively due to the increased attractive interaction between the metal surface and the carbyne body. This result further evidenced our aforementioned analysis of the carbyne formation. The formation energy of the end of carbyne are E_{end} = 0.69, 0.20, 0.02 and 0.02 eV/end for Cu(111), Ni(111), Rh(111) and Ru(0001), respectively. All these numbers are significantly lower than the formation energy of carbyne free end in vacuum (3.5 eV/end), demonstrating the carbyne end is effectively passivated by these transition metal surface. Both the metal-carbyne interaction strength and the carbyne end passivation follow a similar trend, indicating that the activity of these metal surfaces follow the order of Cu(111) < Ni(111) < Rh(111) ~ Ru(0001). This is exactly the same as that for the interactions between carbon monomer/dimer/cluster/graphene edge and the metal surface.

The different C-M interaction strength impacts the electronic structure of carbon chain and hence the formation energy. From Fig. 2d, we can see that an odd-even rule was observed for carbyne formation on Cu(111) surface only. For carbyne formation on Cu(111) surface, energies of even-numbered carbynes are mostly lower than the fitted line while the odd-numbered carbyne have higher energies. A similar rule has been reported for carbon chain formation in vacuum and was explained as a consequence of the polyynic structure. The similarities indicates that the carbyne on Cu(111) surface has very similar electronic structure as that of the freestanding one. Thus it reserves the intrinsic properties of free carbyne, such as the polyynic formation or the alternative single-triple bonds. However, on Ni, Rh and Ru surface, the odd-even difference disappears because of the polycumulenic carbynes are formed and all the π electrons in polycumulenic carbyne can be regarded as well paired no matter the carbyne is odd or even-numbered.

It's worth to note that the C-M interaction also affects the relative stability between carbyne and C monomer. Very strong C-M interaction leads to very stable C monomer formation on the metal surface and therefore a carbyne tends to be dissociated into C monomers. As shown in Fig. 2e, the formation energy per atom of a carbon chain on Cu and Ni surfaces is less than that of a carbon monomer, indicating that C monomers tend to aggregate to carbyne on them. In contrast, on Ru and Rh surfaces, the C monomer has lower formation energy than carbyne, which implies that the carbyne can only be formed only at a higher concentration of carbon monomers. Therefore, carbyne formation on those catalyst with weak C-M interaction, such as Cu, Ni Au, Ag, should be observed easier than on that on very active catalyst surfaces, such as Rh and Ru, Ir.

Certainly the one dimensional carbyne can't be always the ground state structure with the increase of carbon atoms because the sp^1 hybridized C is less stable than the sp^2 hybridized C by ~ 0.9 eV/atom. At large size, the sp^2 hybridized C network will becomes the ground state eventually. In relative to the sp^2 network, the carbyne has the advantage of less dangling bonds (only two at both ends) but such an advantage becomes less and less dominated at large size. As can be seen from Fig. 3, the sp^2 carbon network on Cu(111) surface becomes more stable than carbyne at N_c = 13, where N_c indicates the critical size of structural transition. The critical sizes is reduced to 12, 10, 10 for Ni(111), Rh(111) and Ru(0001), respectively. It should be noted that metal step on the catalyst surface will further stabilize both carbyne and the sp^2 carbon networks, and the transition size from carbyne to network will becomes smaller.[19] Thus the metal step is less favorable for the formation of longer carbyne formation.

The above analysis clearly indicates the high stability of carbyne on metal surfaces in the size range of N < 10-13. This indicates that the two types of carbyne can be observed on the Cu and Ni surfaces. On those metal surfaces which are less active (such as Au, Ag and Cu), polyynic carbyne should be the ground state. While, on those active metal surfaces (such as Ni, Co, Pt, Pd, etc), the polycumulenic carbyne is more stable. In addition to the direct observation of carbyne, the measurement of the superior properties is possible as they can be stabilized on the metal surface for a long time. To motivate the experimental study on the formation of carbynes on metal surfaces, we simulated the STM images of carbynes with 7 carbon atoms on Cu(111) and Ru(0001) surfaces (Fig. S4).

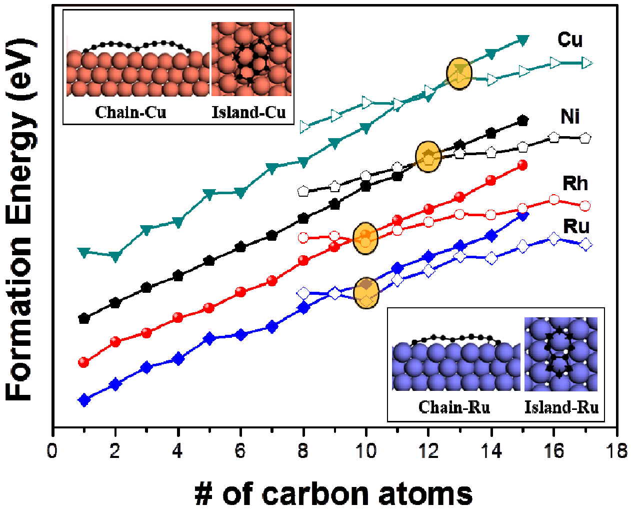

Fig. 3 Structural transition from carbyne to sp^2 carbon network on Cu(111), Ni(111), Rh(111), Ru(0001) surfaces. The critical size on Cu, Ni, Rh and Ru surfaces are 13, 12, 10 and 10, respectively.

Besides the potential observation and measurement of the carbyne, we would like to propose a route to form graphyne by self-assembly of the carbynes on transition metal surface. Given that carbyne is the ground structure under a reasonable size, it is possible to obtain carbynes on some metal surfaces with a high concentration through carbon cluster sputtering at low temperature. Those linear carbyne chains will start to diffuse on the metal surface as the temperature is elevated. If two carbynes with different orientations meet with each other, the active end of one carbyne will bind to a body atom of another carbyne (insert of Fig. 4), resulting in a formation of three carbon chains linked by one sp^2 hybridized carbon atom. The newly formed carbon structure may serve as a nuclei and be attached by more carbon chains and gradually becomes a large network like graphyne domain linked by some sp^2 hybridized carbon atoms (Fig. 4).

As discussed above, the formation of graphyne on catalyst surface is highly depend on the activity of the catalyst surface. On those catalyst surfaces with weak C-M interaction strength, long carbon chain tends to be formed and thus graphyne is expected to be produced easily. However, on those catalyst surfaces with very strong C-M interaction strength, the carbon chain may tend to dissociate and hence the graphyne can be hardly synthesized. This analysis is in agreement with the recent observation of graphdiyne on Cu.[27] Applying same analysis, it is expected that graphyne or graphdiyne should be easily formed on other less active metal surfaces, such as Au, Ag, etc., as well.

For practical experimental design, besides the catalyst surface, many other parameters, such as the temperature, carbon precursor and the coverage of the carbyne will also play important roles. As known from previous calculations,[17] the diffusion barriers of the carbyne chains on the metal surfaces are normally less than 1.0 eV and thus the annealing or self-assembly of the carbyne could be very quick at elevated temperature, thus reasonably low temperature (e.g., ~ 77K) is required for the synthesis of graphyne. At such an temperature, the formation of partially dissociated benzene ring probably could be stable as well and thus mixing with benzene precursor may leads to the formation of graphdiyne as that synthesized on Cu before. Certainly, large coverage of the carbyne will leads to very compact carbon formation which might be very disordered and thus the low coverage should be more preferred for the synthesis of graphyne.

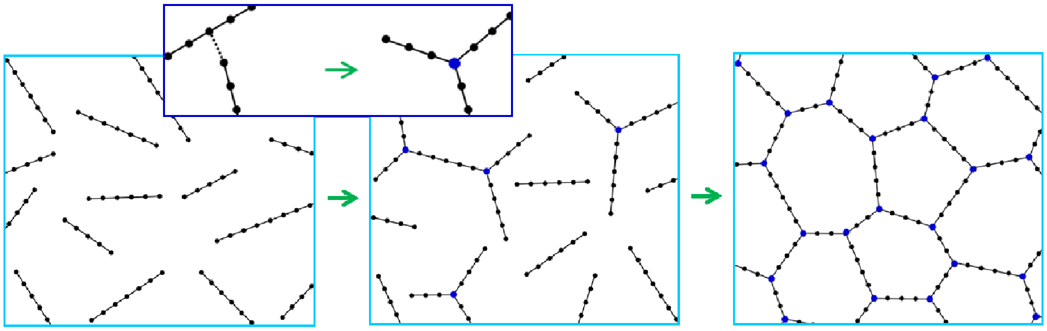

Fig. 4 Illustration of graphyne formation on a transition metal surface by the self-assembly of the carbyne chains.

Conclusions

In conclusion, via density functional calculations, carbyne with size of N < 10-12 is predicted as the ground state of carbon clusters on various transition metal surfaces. Two different carbynes, polyyne and polycumulene, are found to be formed on less active (e.g., Cu) and active (e.g., Ni, Rh, Ru) metal surfaces, respectively. The polyynic carbyne tends to be curved up on the less active metal surface while polycumulenic carbyne prefers to be formed in a straight line on the active metal surface. Beyond the critical size of 10-12, the carbyne structure becomes less stable than the sp^2 carbon network. Thus the carbyne should be observed at low temperature and low carbon coverage. This study provides an effective route to observe the stable carbyne formation on metal substrate and measuring the intrigue properties of carbyne. Moreover, we proposed a route to form graphyne on transition metal surface by the self-assembly of the carbon chains.

Acknowledgements

The work was supported by NSFC grants (21303056 and 21273189), hong Kong GRF grants (B-Q35N and B-Q26K) and Shanghai Pujiang Program (13PJ1402600).

Notes and references

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Electronic Supplementary Information (ESI) available: [Computational details of and structural information of carbon chain on Ni(111) and

Rh(111) surfaces, carbon island on Cu(111), Ni(111), Rh(111) and Ru(0001) surfaces.]. See DOI: 10.1039/c000000x/

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