Study of the interaction between copper and carbon nanotubes

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Abstract

Copper deposited by thermal evaporation onto pristine and oxygen plasma treated carbon nanotubes (CNTs) diffuse over the CNT surface, coalescing and forming crystalline islands. The nucleation sites of the islands are preferentially defects, and more homogeneous island dispersion was observed at the CNT oxygen functionalized surface. The presence of weakly bound oxygen atoms at the CNT surface induces the formation of Cu–O bonds at the Cu/CNT interface, as described through density functional calculations. Exposure to air allows further oxidation to facetted crystalline Cu2O. Oxygen plasma pretreatment represents a promising route for homogenous disperse Cu2O nanoparticle decoration of CNTs.

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The increasing interest in the interaction between metal atoms and carbon nanotube (CNT) surfaces arises from the important role of the CNT–metal junction in the integration of CNTs in applications such as electronic devices [1,2], nanocomposite materials [3–6], and catalytic systems [7]. The Cu–CNT system is of importance for thermal conductance applications [8]. Copper oxide nanoparticles have been shown to form Cu2O below 25 nm diameters [9,10], which have been used for water splitting and other catalytic processes [11], gas sensing applications [12], and are of great interest for photovoltaic applications due to their intermediate direct bandgap of ~2.2 eV [11,13]. For such applications an efficient charge transfer scaffold such as that provided by carbon nanotubes is desirable. For all of these applications a detailed characterisation and understanding of the copper–CNT interface is critical.

The binding energy between CNTs and metals can be efficiently tuned by grafting reactive chemical groups at the CNT surface. Reports show improvements in the dispersion of CNTs in different matrices and in the tuning of the CNT–metal junction properties [14,15]. The presence of oxygen at the interface between CNTs and Cu was reported to improve interfacial strength [16]. We recently showed that the interaction of Au [17], Rh [18], and Ti [19] with CNTs was influenced by the presence of oxo-groups grafted at the CNT surface. The presence of the uniformly grafted oxo-groups improved the dispersion of Au and Rh clusters while at the Ti–CNT interface it reduced the net charge transfer from Ti atoms to the CNT, leading to partial de-bonding of the metal.

In this Letter, we study the Cu–CNT interaction by analysing multi-walled carbon nanotubes (MWCNTs) decorated with clusters produced by thermal evaporation of Cu atoms. Different amounts of Cu were evaporated onto the surface of pristine and oxygen plasma treated MWCNTs, which were analysed using transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The experimental results were compared to density functional (DFT) calculations of the interaction between Cu atoms and pristine and defective graphene. We first studied the morphology of the Cu/CNT samples. The HAADF–STEM images of the Cu/CNT samples show that thermally evaporated Cu atoms nucleate onto the CNTs forming clusters (Volmer–Weber growth mode) on both the pristine and oxygen functionalized CNT surfaces (Figure 1a and b). The Cu islands are more homogenously dispersed on the oxygen functionalized CNT surface than on the pristine CNT surface, indicating that the oxygen plasma treatment creates well-dispersed nucleation sites. HRTEM analysis shows that highly crystalline facetted nanoparticles are formed on both pristine and oxygen functionalized CNT surfaces (Figure 1c and d).

In order to understand cluster formation at the CNT surface we modelled Cu–graphene interaction. A single Cu atom on graphene binds weakly above the centre of a C–C bond, with binding energy of only 27.0 kcal/mol (Cu–C distances of 2.06 Å), consistent with previous DFT–LDA calculations [20]. The binding energy of Cu above atom sites or hexagonal voids in the graphene is within 1.15 kcal/mol of the above-bond site. Indeed the energy difference between the above-atom and above-bond sites gives a maximum for the migration barrier of only 0.70 kcal/mol, i.e. Cu atoms are more surface mobile on graphene than Au, Ag, Pt, Pd, Rh, Ni, or Ti [19,21,22].
To compare the relative strength of Cu–C and Cu–Cu interactions we placed four Cu atoms epitaxially above graphene hexagon-centre sites in either a flat parallelogram or pyramidal configuration. The difference in these two configurations lies in the bonding of the fourth Cu atom which in the pyramidal configuration forms three Cu–Cu bonds but no bonds with the graphene, while in the parallelogram arrangement forms only two Cu–Cu bonds but lies in proximity to the graphene. Thus this evaluation allows comparison of Cu–Cu and Cu–C bonding and serves as the smallest cluster size test for clustering or wetting of the tube surface.

The pyramidal arrangement binds with an energy of 58.34 kcal/mol atom, 6.92 kcal/mol more stable than the parallelogram (see Figure 2a). The preference for Cu–Cu over Cu–C bonding confirms the Volmer–Weber growth mechanism, i.e. on pristine surfaces, highly mobile Cu atoms will exhibit poor wetting and will rapidly aggregate into Cu nanoparticles.

A single Cu atom binds strongly to an isolated graphene vacancy (119.22 kcal/mol compared to an isolated Cu atom, i.e. 92.22 kcal/mol stronger than to pristine graphene). Cu sits 1.336 Å above the basal plane, with two shorter C–Cu bond lengths of 1.829 Å and one slightly longer at 1.832 Å (see Figure 2b). The defect has a net spin of 0.95\textmu B due to the missing p\textsubscript{z}-orbital associated with the missing carbon atom. While there is no C–C bond reconstruction (as seen in a pristine undecorated graphene vacancy) the defect retains some asymmetry in the Cu–C bonding. Spin for the Cu-vacancy centre has also been observed in previous calculations although the binding energies found were lower at \(\sim 9\) kcal/mol and C–Cu bond lengths longer \(\sim 1.87\) Å, consistent with the use of the generalised gradient approximation (GGA) [23]. Thus pristine vacancies will act as strong traps for surface mobile Cu. However, nanotube vacancies spontaneously oxidise when exposed to air [24–27] and thus a realistic model for vacancy interaction with Cu should include oxygen.

We next examined the interaction of a single Cu atom with an oxygenated monovacancy (Vac\textsubscript{O\textsubscript{2}}). We optimised multiple structures with different starting geometries. The most stable structure we obtained was with Cu above the bond centre of a backbond of the C–O–C ether group in the vacancy (see Figure 2c). In this case the Cu binding to the Vac\textsubscript{O\textsubscript{2}} is 36.90 kcal/mol compared to Cu on the pristine basal plane, i.e. there is a strong interaction and Cu atoms will be pinned at oxidised vacancy sites. This suggests oxygenated vacancies will act as nucleation sites for Cu aggregation. Cu–C bond lengths are 1.99 and 2.06 Å, with strong interaction between Cu and the ketone oxygen (Cu–O distance of 1.86 Å). The ether oxygen is forced away (displaced out of plane on the other side of the graphene sheet) at 2.71 Å from the Cu. Unlike the pristine Vac–Cu complex, the Vac\textsubscript{O\textsubscript{2}}–Cu complex has no net spin.

The modelling suggests that these oxidised defects will promote metal nucleation due to strong metal pinning. In order to verify this assumption we induced experimentally the formation of oxidised defects at the CNT surface. By oxygen plasma treating weakly defective CNT surfaces, oxidised defects can be created reproducibly. The oxygen plasma treatment induces the grafting of oxo-groups at the CNTs surface as a result of processes such as O\textsuperscript{2−} dissociation on vacancies created during the plasma treatment [25]. XPS analysis shows that after Cu evaporation the intensity of a broad structure centred at 287.5 eV attributed to photoelectrons emitted from carbon atoms belonging to oxo-groups at the CNTs surface as a result of processes such as O\textsuperscript{2−} dissociation on vacancies created during the plasma treatment [25].

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intensity from oxygen-related C 1s satellite peaks. Comparison of the O 1s XPS spectra recorded before and after Cu deposition reveals a new chemically shifted component at the high-energy side of the peak (Figure S2), indicative of interaction of the Cu clusters with oxygenated defects. This confirms that the improvement in Cu island dispersion for the plasma-treated CNTs is associated with the presence of homogeneously distributed oxidised defects at the CNT surface and can be linked to the increased number of nucleation centres. However, the kinetic energy of the C 1s photoelectron excited with photons of 3.5 keV is ca 3.2 keV (corresponding to an inelastic mean free path (IMFP) of ~90 Å) [28]. This means that at the low Cu coverages considered in this Letter, the significant intensity decrease in the C 1s satellite structures is unlikely to be associated only to the increase of the amount of Cu evaporated onto the CNTs. A second possible cause for the reduction in the oxygen-related C 1s satellite peaks in the XPS is the formation of bonds between O and Cu at the expense of carbon–oxygen bonds. Equally, C–O–Cu bonding will change the screening of the C–O bonds, thereby changing the binding energy of their C 1s levels. Thus the photoelectrons emitted from these atoms will no longer contribute to the signal. The chemically shifted component in the O 1s spectrum is consistent with a strong C–O–Cu interaction (Figure S2).

A final possibility is gettering in which the Cu atoms capture oxygen from the CNT surface. In order to test this we optimised several VacO2–Cu structures with the oxygen no longer bound directly to the vacancy site. However such structures were energetically unstable (nearly 90 kcal/mol less stable than the VacO2–Cu structure described above), i.e. low density Cu seems unlikely to capture oxygen out of tightly bound vacancies (120 kcal/mol [29]) spontaneously.

In order to investigate oxygen gettering and possible surface layer oxides at higher Cu concentrations, we next modelled an epitaxial bilayer of Cu on graphene, and introduced oxygen at different positions in the structure. We emphasise that this calculation is not intended to represent experimental copper oxide structures but serves purely as a comparative study to identify trends in oxygen behaviour. A $2 \times 2$ unit cell was used, i.e. 8 atoms of C, 3 Cu atoms per layer (6 total), and 1 oxygen atom. The oxygen was placed in different locations, and oxygen on the Cu exterior surface is strongly thermodynamically favoured. Placing it between the Cu layers is 54.65 kcal/mol less stable than on the surface, and between the Cu and the graphene is 116.92 kcal/mol less stable than on the Cu surface (see Figure S3). This suggests that oxygen not strongly covalently bound to the carbon will be rapidly gettered and drawn to the Cu surface. This intriguing effect suggests a ‘self-cleaning’ mechanism for the Cu–C interface, which could also contribute to the reduction in the structure related to the oxygroup in the XPS intensity. Experimentally such an effect will ultimately result in the formation of copper oxide.

To evaluate the formation of CuO clusters inside the analysis chamber due to the gettering of weakly bound oxygen from the CNT surface, the Cu 2p and Cu L3VV spectra for a range of copper coverages deposited onto the pristine and oxygen plasma treated CNTs are analysed (Figure S4). Unresolved in XPS, signals associated to copper and copper oxides can be separated in X-ray excited Auger electron spectroscopy (XAES). The L3VV spectrum of metallic Cu is known to have characteristic kinetic energy peaks at 919.7 and 922.3 eV [30]. In the Cu (L3VV) spectra recorded after 1 angstrom of Cu evaporation on pristine and oxygen plasma functionalized CNTs (Figure S5), no such structure is observed. The lack of observation implies copper oxide formation. For increasing amounts of Cu evaporation the shape of the Cu (L3VV) spectrum evolves to that of CuO L3VV suggesting that whereas Cu–O bonds are formed at the Cu/CNT interface due to the presence of oxidised defects, subsequently deposited copper remains metallic (Figure S4b), which is also supported by the broadening of the oxygen peak after the copper evaporation. Based on these observations, we suggest that Cu–O bonds are formed at the interface due to the getter effect, however when the available (weakly bound) oxygen is completely consumed the growth proceeds as copper metal.

Following these spectroscopy investigations we subsequently removed the samples from the vacuum chamber and transferred them for HRTEM study (Figure 1c and d). Here the crystalline structure corresponds to cubic CuO, similar to previous observations for Cu oxide nanoparticles [9], showing that air exposure is suffi-

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**Figure 2.** Density functional optimised structures for (a) Cu tetrahedron over graphene, (b) copper bound to a single pristine monovacancy, and (c) copper bound to an oxygenated monovacancy (VacO2–Cu). Copper atoms are small red spheres, oxygen atoms large red spheres, carbon atoms grey spheres. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
cient to complete the oxidation process to the stable oxide form for 
Cu nanoparticles of this size \[9\]. Unlike other metals we have studied (Au, Ag, Ni, and Rh) these particles are strongly faceted, due to 
the high surface stability of certain crystallographic Cu$_2$O planes 
such as (111) \[31\]. We note that any residual subnanometric 
CuO shell will be difficult to detect via HRTEM \[10\].

In conclusion, copper atoms thermally evaporated onto CNTs 
diffuse rapidly on the surface, forming discrete highly crystalline 
faceted particles rather than a continuous amorphous layer, de-
spite moderate surface interaction. Our calculations show that Cu 
has a higher surface mobility than most metals such as Au, Ag, 
Pt, Pd, Rh, Ni, and Ti. While it interacts strongly with oxygen and 
has a higher surface mobility than most metals such as Au, Ag, 
Pt, Pd, Rh, Ni, and Ti. While it interacts strongly with oxygen and 
appears to getter oxygen from the basal plane, it is unable to scav-
enge oxygen from oxygenated vacancy sites. Oxygen plasma treat-
ment in a RF-plasma grafts oxygen to the CNT surface, creating 
cluster nucleation sites. After exposure to air the Cu nanoparticles 
restructure to Cu$_2$O, showing this to be a promising route for for-
cluster nucleation sites. After exposure to air the Cu nanoparticles 

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Appendix A. Supplementary data

Details on theoretical and experimental methods, C 1s spectra 
recorded on pristine, oxygen functionalized CNTs and Cu coated 
oxogen functionalized CNTs (Figure S1) and Cu (L3V, V) Auger 
electron spectra recorded on the pristine and on the oxygen plasma 
functionalized CNTs (Figure S2) are given, and calculated epitaxial 
Cu layer structures on graphene (Figure S5). Supplementary data 
associated with this article can be found, in the online version, at 
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References

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