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Probing the interaction between gold nanoparticles and oxygen functionalized carbon nanotubes

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ABSTRACT

The interaction between evaporated gold and pristine or oxygen plasma treated multi-walled carbon nanotubes (MWCNTs) is investigated. Experimental and theoretical results indicate that gold nucleation occurs at defect sites, whether initially present or introduced by oxygen plasma treatment. Uniform gold cluster dispersion is observed on plasma treated carbon nanotubes (CNTs) and associated with the presence of uniformly dispersed oxidized vacancy centres on the CNT surface.

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1. Introduction

Gold is considered the most inert of all metallic elements [1]. However, nanosized Au particles can show catalytic activity [2,3]. It has already been demonstrated that supported Au catalysts can exhibit high catalytic activity for reactions such as the selective oxidation of CO in hydrogen stream [4], selective oxidation of hydrocarbons and CO [5], epoxidation of propene [6], and selective hydrogenation of unsaturated aldehyde and ketone [7]. The study of Au catalysts on different supports (such as metal oxides TiO₂ [8], CeO₂ [9], Al₂O₃ [10], and ZrO₂ [11], etc.) has revealed that the catalytic activity of supported Au depends significantly on the size of Au particles and is markedly influenced by the interaction between Au and the support.

Carbon nanotubes (CNTs) have been heralded as a very attractive support for catalytically active materials due to their unique metal/support interaction resulting in distinct catalytic behavior [12]. Their surface chemical stability significantly reduces unwanted side reactions, while their good

thermal conductivity reduces temperature gradients. Their high aspect ratio results in large active specific surface areas, which increases the contact surface between the reactants and active phase, while the lack of porosity prevents diffusion of products into the bulk [12]. The first catalytic studies conducted on CNT-supported metal catalysts such as Rh, Pt and Pd have shown encouraging results in terms of activity and selectivity in a large variety of reactions [13,14]. In particular, high activities and selectivity have been obtained in hydrogenation reactions [13] and electrocatalysis [14] as compared to classical supports.

Previous theoretical studies have examined the interaction of single Au atoms with the perfect graphitic surface [15,16] or of an infinite metallic trilayer with graphene and nanotubes [17–20]. They all conclude that Au interacts more weakly with the graphitic surface than other metals such as Ti or Pd. However, none of these studies looked at defective surfaces. Oelhafen et al. used X-ray photoemission spectroscopy (XPS) and grazing incidence small-angle X-ray scattering to show that Au atoms interact weakly with highly-oriented pyrolytic

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graphite (HOPG) and, depending on the density of defects at the carbon substrate surface, the metal nanoparticle growth can be mediated by their presence [16,17].

A better understanding of metal–nanotube interaction will have significant impact on the engineering of new applications such as catalysis. In the current work we study the interaction between pristine and plasma treated CNTs with Au particles. Samples were prepared by thermal evaporation of Au atoms onto pristine and plasma functionalized CNTs. The dispersion, shape and size of clusters were quantified by high resolution transmission electron microscopy (HRTEM). Au–CNT interaction was probed by high-energy X-ray photoelectron spectroscopy (XPS), and results are compared to density functional theory (DFT) calculations.

2. Method

The samples contained multi-walled carbon nanotube (MWCNT) powder synthesized via chemical vapour deposition (CVD). The oxygen functionalization was performed in a home made chamber using inductive coupled plasma at a RF frequency of 13.56 MHz [21]. Samples for XPS and HRTEM were treated simultaneously. For XPS analysis the MWCNT powder was supported on a copper conductive tape suitable for ultra high vacuum. For TEM analysis the CNT powder was dispersed in ethanol, and the solution was dropped onto a lacey carbon film supported by a copper grid. The samples were exposed to the plasma on their support to prevent contamination occurring during manipulation. Once the sample was placed inside the plasma glow discharge, the treatment was performed under a gas pressure of 13 Pa, 15 W power, and 60 s treatment time.

XPS measurements were performed at the BW2 beamline in Hasylab (Hamburg) using a photon energy of 3300 eV [22–24]. The Au 4f_{7/2} peak at 84 eV recorded on a reference sample was used for calibration of the binding energy scale. In order to check for any possible photon energy drift during the measurements reference spectra were recorded before and after each data set recorded on all samples.

An electron beam was used to evaporate gold. A quartz balance was used to calibrate the amount of evaporated Au. Nominal deposition amounts quoted in the paper are obtained by extrapolation from calibrated thick deposition measurements. Sample transfer from the preparation to the analysis chamber was carried out while maintaining UHV conditions, the residual pressure in the analysis chamber remaining below 1×10^{-8} Pa.

HRTEM was performed using a Philips CM30 microscope operated at 200 kV.

DFT calculations within the local density approximation [25] are carried out on an 8×8 supercell of graphene, i.e. a monolayer of 128 carbon atoms. Graphene was chosen as a reasonable approximation for a large diameter MWNT surface. Fully spin polarized single *k*-point calculations were geometrically optimized from multiple possible starting structures. Hartwigsen, Goedecker, and Hutter (HGH) relativistic pseudopotentials [26] were used for all atoms. Atom-centered Gaussian basis functions are used to construct the many-electron wave function with angular momenta up to

$l = 2$. Electronic level occupation was obtained using a Fermi occupation function with $kT = 0.04$ eV. In the energetic analysis that follows, binding energies are defined as the difference in energy between the relaxed combined system (final state) and the isolated perfect graphite sheet plus a single isolated metal atom ($s = 1$) (initial-state), unless otherwise stated. The diffusion barrier for Au was determined by constraining the system symmetry during optimisation and was confirmed as a saddle point by subsequent symmetry breaking and structural optimisation, which led to the ground state structure.

3. Results and discussion

To ensure that the same amount of gold was evaporated on each pair of samples, metal evaporation was performed simultaneously onto pristine and oxygen plasma treated CNT surfaces. It can be observed from Fig. 1 that plasma treatment improves the cluster dispersion and reduces the size of Au particles. On HOPG, Au nucleation is characterized by diffusion limited aggregation, whereas if the surface defect density is high the growth is influenced by nucleation taking place on defect sites [15]. The diffusion constant is therefore reduced with respect to pristine HOPG and a higher density of small particles can be found on the surface [15]. Considering the similarities between HOPG and CNT surfaces, the improved Au cluster dispersion at a plasma treated CNT surface can be associated to the presence of a higher density of active sites for nucleation created during the plasma treatment. The inset of Fig. 1a shows a magnified image of a Au cluster sitting at the CNT surface, from this the typical spherical shape of the Au clusters can be observed.

Our calculations show that a single Au atom bonds to a pristine graphitic layer with binding energy of 0.66 eV. The structure has a net magnetic moment of $0.99 \mu_B$. The Au atom sits above a carbon atom at a distance of 2.26 Å. This is in agreement with values found in the existing *ab initio* literature: for example a single Au atom on an (8,0) single-walled nanotube was found to have carbon–Au distance 2.2 Å, binding energy 0.5 eV, and magnetic moment $1.02 \mu_B$ [27]. Literature values of this binding energy for small nanotubes vary with carbon sheet curvature, finding higher binding energies for smaller diameters (e.g. decreasing the nanotube diameter from 8.14 to 6.27 Å increases the Au binding energy by 0.2 eV [27]). Since the MWNTs we use experimentally have diameters from 60 to 200 Å, large graphene supercells are the most appropriate.

Although the binding of a single atom with the perfect graphitic layer is weak – compared with the binding energy of Ti to graphene, which is 1.81 eV [20] – it increases to 1.07 eV when the Au atom is next to an oxygenated vacancy (VacO₂) and to 1.16 eV when next to an oxygenated divacancy (Vac₂O₂). These centres have no net spin. Further comparison of binding behavior of Au on pristine tubes with other metals is made elsewhere [28].

Our calculated barrier for Au diffusion on the graphitic surface is 0.1 eV. A simple first order Arrhenius type equation with the Debye attempt frequency (10^{13} Hz) suggests that isolated Au atoms on the graphitic surface at room temperature

Fig. 1 – Au clusters formed on CNT surfaces after a nominal Au evaporation of 5 Å (a) pristine MWCNTs. The inset shows a higher magnification image with a typical cluster. (b) Oxygen plasma treated CNT. The inset shows the particle radius distribution.

will be moving at more than 2×10^{11} hops/second. However, when attached to a VacO₂ the lower limit barrier to leave the defect site is 0.51 eV (see Fig. 2) which corresponds to 2×10^4 hops/second at room temperature. Thus the dwell time for Au at oxygenated defects will be significantly higher than on sections of pristine CNT, and hence oxygenated defects will trap Au atoms for long enough to reduce their mobility and act as nucleation sites.

Oxygen plasma treatment was reported to graft C=O and C–O–C functional groups at the CNTs surface as a result of processes such as O₂⁺ dissociation on vacancies created during the plasma treatment [29]. Calculations suggest that Au nucleation centres occur in the proximity of oxygenated de-

fects created by the plasma treatment. Therefore, the improved Au cluster dispersion for the plasma treated MWCNTs can be associated with the presence of dispersed oxidized vacancies at the CNT surface.

The change in the chemical nature of the CNT surface caused by exposure to the oxygen plasma was evaluated by analyzing the kinetic energy of photoelectrons generated by photons of energy equal to 3300 eV. Fig. 3 shows the comparison between the C 1s peaks recorded from pristine, oxygen plasma treated MWCNTs and Au coated oxygen functionalized CNTs.

The chemical modification produced by the plasma treatment can be identified by a broad structure peaking at

Fig. 2 – Plot showing the DFT calculated binding energies (in eV) and barriers for Au to graphene, oxygenated divacancy (Vac₂O₂) and oxygenated vacancy (VacO₂).

Fig. 3 – Comparison of the C 1s spectrum recorded on pristine, oxygen plasma functionalised CNT (f-CNT) and Au coated f-CNT. The nominal amount of evaporated Au is 5 Å.

287.5 eV; it is attributed to photoelectrons emitted from carbon atoms belonging to hydroxyl (component centered at 286.2 eV), carbonyl or ether (component centered at 287.2 eV) and carboxyl or ester groups (component centered at 288.9 eV) [30]. The evaporation of Au atoms onto the CNTs reduces the effective number of C 1s and O 1s photoelectrons contributing to the XPS spectra, resulting in a decreased intensity; during the onset of the evaporation the decrease in the O 1s core level intensity was found to be more pronounced than the C 1s, supporting our previous suggestion that Au nucleation centres occur mainly in the proximity of oxygenated defects created during the plasma treatment (Fig. 4). Two effects can be associated with the decrease in intensity in the O 1s core level peak: Au atoms nucleating near oxygenated defects would cover first the oxygenated sections;

Fig. 4 – Au 4f peak recorded (a) on bulk Au sample, (b) pristine CNT after 0.1 Å of Au evaporation, (c) oxygen plasma functionalized CNT after 0.1 Å Au evaporation.

consequently the contribution of photoelectrons emitted from oxygen atoms localised under the Au clusters to the O 1s core level peak is expected to be smaller. However, the kinetic energy of the O 1s photoelectron excited with photons of 3300 eV is ca. 2800 eV (corresponding to an inelastic mean free path (IMFP) of ca. 80 Å), therefore at the low Au coverages considered in this work, a significant intensity decrease in the O 1s peak is not expected. Fig. 1 shows typical Au cluster formation at the CNT surface after a nominal evaporation of 5 Å of Au. This amount of evaporation leads to the formation of Au clusters with average height of 28 Å. This height is smaller than the IMFP for photoelectrons with kinetic energy of 2800 eV, thus another effect should be considered to explain the pronounced decrease observed in the O 1s peak intensity at low Au coverages. An alternative explanation for this pronounced decrease is that it may be due to the removal of the oxygen species weakly bound to the CNT surface by the Au atom, whereas with a binding energy of ca. 5 eV [27] all oxygen atoms bound to carbon vacancies will remain in place.

This alternative interpretation is supported by our calculations. When we examine a single oxygen atom bonded to the pristine graphene plane it adopts an epoxide-type configuration above a carbon–carbon bond. Such a configuration, although metastable, is endothermic compared to O₂ in the gas phase, i.e. the addition of a second oxygen atom leads to the formation and desorption of an oxygen molecule. This situation changes in the proximity of oxygenated vacancies, where such epoxide-bonding can become weakly exothermic [30]. If we introduce a Au atom to the epoxide-bonded oxygen on pristine graphene, the Au–O pair spontaneously lifts off the sheet to sit above the π -cloud, i.e. the Au cleans the oxygen from the basal plane. Presumably this will also occur for epoxide oxygen in the proximity of oxygenated vacancies. However oxygen bonded directly to the vacancy is too strongly bound and will remain. Thus we would expect initial Au addition to oxygen plasma treated CNTs to remove any residual epoxide-bonded oxygen remaining on the nanotube surface, while leaving oxygen present in vacancy centres. The contribution of each of these effects to the observed decrease in the O 1s intensity during the onset of the metal evaporation is still under investigation.

Fig. 5 shows the comparison of Au 4f spectra recorded after a nominal evaporation of 0.1 Å Au onto pristine and oxygen plasma functionalized CNTs with a Au 4f spectrum recorded on a bulk Au sample. The Au 4f peaks recorded on the Au decorated CNTs shift towards higher binding energy and their FWHM is notably larger. Three main factors can contribute to the core level binding energy shift in photoemission: initial-state effects associated to changes in the local electronic-structure, final state effects due to changes in the relaxation process (extra-atomic response to the positively charged photohole), and cluster charging [31–33]. Changes in the electronic configuration due to formation of different chemical states at the cluster/CNT interface can be ruled out as inspection of the C 1s peak and O 1s peak did not show any additional feature. Thus no strong bond formation between the Au and carbon atoms or oxygen atoms can be claimed. For supported clusters, a poor electrical contact between the clusters and the substrate hinders the electron flow to screen the hole created during the photoionization process

Fig. 5 – Au 4f core level spectrum recorded on oxygen plasma treated CNTs after 0.1 Å of Au evaporation (blue) and result of its analysis. The doublet peak components (labeled as 1, green) are generated by photoelectrons emitted from small metallic Au particles. The component labeled as 2 (red) can be associated with photoelectrons emitted from Au atoms in metal clusters. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

[34,35]. As a consequence, the cluster remains positively charged during the photoemission process due to the photo-hole left behind by the emitted photoelectron. The Coulomb interaction reduces the kinetic energy of the photoelectron, which therefore appears at a higher binding energy in the spectrum. This effect increases with decreasing cluster size – i.e. with decrease in the coordination number of Au–Au nearest neighbours leading to a decrease in the density of electronic states near the Fermi energy level (Fig. 6).

The influence of the factors described above on the core level binding energy depends on the nature of the cluster (i.e. the chemical composition, shape, size, area and strength of interaction with the support) and on the nature of the support. The observed shift may be explained as resulting purely from a change in the final state relaxation, however based on the current photoemission results alone we cannot unambiguously differentiate between initial- and final state effects [36,37].

A close inspection of the Au 4f peaks shows that the spectrum recorded on the plasma functionalized sample can be decomposed into two components that can be fitted by two doublets, using Doniach–Sunjic profiles [33]. The inset of Fig. 1b shows that the size distribution of the Au clusters formed at the CNT surface is better represented by a bi-modal-like distribution, hence it can be suggested that these two doublets are associated to the presence of a bi-modal distribution of Au cluster size – the Au 4f doublet at lower binding energy would be generated by photoelectrons emitted from the larger clusters while smaller clusters give rise to the doublet at higher binding energy. It is important to point out that, from the DFT analysis different barriers were found for Au diffusion on a plasma functionalized surface (0.1 eV for pristine,

Fig. 6 – Variation of the C 1s and O 1s core levels peak intensity for increasing amounts of Au evaporated onto CNTs – the lines are a visual guide only.

0.51 eV to leave the VacO₂ defect site and 0.6 eV to leave the Vac₂O₂ defect site). Therefore, from the discussion above, it can be suggested that large particles nucleate and grow on surface regions with high atom mobility (barrier diffusion 0.1 eV) while the smaller particles would form near the oxidized vacancies (barrier diffusion 0.51–0.61 eV). The existence of at least two barriers with very different energy can explain the bi-modal size distribution of Au clusters as a consequence the double component in the Au 4f spectra. We note that the calculations show a relatively small capture cross-section for the VacO₂ centres; placing a Au atom at a distance of further than 10 Å from the VacO₂ showed negligible binding.

4. Conclusion

We have examined the bonding of thermally evaporated Au atoms onto pristine and oxygen plasma functionalized CNTs via HRTEM and HRXPS. Our DFT calculations suggest that Au nucleation centres will occur in the proximity of oxygenated defects. We therefore associate enhanced Au cluster dispersion for the plasma treated MWCNTs with the presence of dispersed oxidized vacancy centres on the CNT surface.

The Au 4f XPS spectrum shows evidence of two distinct populations of particle sizes, explained in terms of Au particle nucleation on oxidized or pristine sections of CNT. The preserved structural characteristic of the graphene layer under the Au clusters, combined with the absence of new features in the C 1s and O 1s XPS spectra, testifies to the absence of a mixed phase at the Au cluster–CNT interface.

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