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Solution-phase synthesis of chromium-functionalized single-walled carbon nanotubes

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ABSTRACT

The solution phase reactions of single-walled carbon nanotubes (SWNTs) with $Cr(CO)_6$ and benzene-$Cr(CO)_3$ can lead to the formation of small chromium clusters. The cluster size can be varied from less than 1 nm to about 4 nm by increasing the reaction time. TEM images suggest that the clusters are deposited predominantly on the exterior walls of the nanotubes. TGA analysis was used to obtain the Cr content and carbon to chromium ratio in the Cr-complexed SWNTs. It is suggested that the carbon nanotube benzenoid structure templates the condensation of chromium atoms and facilitates the loss of carbon monoxide leading to well defined metal clusters.

1. Introduction

Organometallic complexation of graphitic surfaces, such as carbon nanotubes and graphene, offers a chemical approach to the design of novel materials of extended dimensionality [1–3]. The extended, periodic π-electron graphitic structures are zero or narrow band gap materials with high lying HOMOs and low lying LUMOs, which enhance the π-electron interactions with the d-orbitals of the transition metals and result in the formation of hexahapto-complexes, in which the benzenoid ring of the graphene layer serves as a ligand.

Initially the organometallic chemistry of carbon nanotubes was focused on atomically bridging the graphene surfaces to extend the dimensionality of the graphene materials [4] and in the case of carbon nanotube films to improve the electrical contacts between individual carbon nanotubes [5–7]. There are two approaches to the synthesis of metal–graphene complexes – the metal vapor synthesis [8–10] and solution chemistry [1,11–15]. Solution chemistry affords the synthesis of a variety of compounds and we discovered that graphitic surfaces can template the formation of metal clusters, because the graphene surface can adjust the electron count in the six-membered rings by fluctuations in the Clar structures (see below) [16]. The cluster compounds are of potential interest as catalysts and sensors [17,18].

Here we report the formation of chromium clusters on single-walled carbon nanotubes (SWNTs) during solution-phase synthesis and the effect of reaction time on cluster size.

2. Experimental

Materials: Purified electric arc produced SWNTs were obtained from Carbon Solutions, Inc (P2-SWNT, 〈http://www.carbonsolution.com〉). All other chemicals were purchased from Aldrich and used without further purification.

Synthesis of Cr-coordination complexes, $(\eta^6\text{-SWNT})Cr_x(CO)_y$: The synthesis was carried out in argon atmosphere using standard Schlenk techniques. The SWNT material (40 mg, 3.33 mmol of carbon) was dispersed in dibutyl ether (15 nm) by ultrasonication (Aquasonic 50HT, VWR Scientific sonic power 75 W, frequency ~40 kHz) for 2 h, and chromium hexacarbonyl (122 mg, 0.56 mmol, F.W.=220.06) was added to the homogeneous suspension. The mixture was degassed with argon for 1 h and then heated to 110 °C. The reactions were conducted over periods of 1 day (24 h), 3 days and 5 days. After reaction, the mixture was

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cooled to room temperature and filtered using a 0.22 μm PTFE membrane and the solid washed with dibutyl ether and hexane to remove unreacted reagents. The product was dried under vacuum in a desiccator overnight in dark to obtain $(\eta^6\text{-SWNT})Cr_x(CO)_y$ as a black solid.

The reaction between SWNTs and $(\eta^6\text{-benzene})Cr(CO)_3$ was conducted for a duration of 5 days using the same procedure.

TGA characterization: TGA data were collected with a Perkin-Elmer Pyris 1 Thermogravi-metric Analyzer at a heating rate of 5 °C/min in air.

TEM: High resolution TEM imaging and elemental analysis using EDS (energy dispersive spectroscopy) were recorded with an FEI Titan 80–300 kV electron microscope, equipped with a monochromator and an image corrector. The microscope was operated at 60 kV to reduce beam damage of the samples; 0.12 nm point resolution was achieved by reducing the energy spread of the electrons to below 0.15 eV with the help of the monochromator and carefully correcting the 3rd order aberration of the objective lens using the image corrector. *Z*-contrast imaging of the chromium clusters on the SWNTs was investigated by STEM with a high angle annular dark-field (HAADF) detector, in which the heavier Cr atoms appear brighter than the atoms in SWNTs.

3. Results and discussion

Synthesis and TGA analysis: The η^6 – complexation reaction between SWNTs and $Cr(CO)_6$ was carried out for 1, 3 and 5 days and the effect of the reaction duration on the amount of Cr deposited on the SWNTs was evaluated by TGA. Fig. 1a shows that the oxidation of the purified SWNTs occurs above 500 °C with two peaks at 570 °C and 699 °C in the derivative of the weight loss curve. The SWNTs contain 4.3% metal (Ni and Y, residual catalyst from the nanotube synthesis). The SWNTs have been purified with a mineral acid; the remaining metal is likely encapsulated in a carbon shell because it could not be removed by further treatment with acid and therefore we anticipate that the catalyst does not affect the Cr cluster synthesis. The material prepared by the 1 day complexation reaction (Fig. 1b) exhibits a weight loss at lower temperatures with a small peak at 270 °C and a predominant peak at 480 °C, due to the presence of Cr. The amount of Cr is 1.6 wt% calculated assuming that the residue consists of Cr_2O_3 and allowing for the amount of Ni- and Y-oxides, present in the starting SWNTs. This corresponds to an atomic ratio of carbon to chromium (C:Cr) of 110:1. The Cr content in the functionalized SWNTs increases to 2.5 wt% after the duration of the complexation reaction is increased to 3 days, corresponding to 1 Cr atom for every 60 carbon atoms (Fig. 1c). The atomic ratio C:Cr decreases to 20:1 for the Cr–SWNT product synthesized by the 5-day reaction (Fig. 1d). A similar C–Cr ratio was obtain for the Cr–SWNT complex synthesized by reacting the SWNTs with benzene-chromium tricarbonyl (Fig. 1e). The development of the peak in the vicinity of 290 °C with increasing chromium content may be attributed to the growth of the chromium clusters and their ability to catalyze the decomposition of SWNTs as they approach the properties of the bulk metal.

TEM characterization of the Cr–SWNT complexes: The chromium-functionalized SWNT materials were examined with high-resolution TEM and representative images are given in Fig. 2. The purified SWNT material comprises nanotubes, which are well graphitized, with an average diameter of ~1.4 nm; some of the remaining carbonaceous impurities are visible as small formations of irregular shape (Fig. 2a). The TEM images of the Cr-complexed SWNTs show

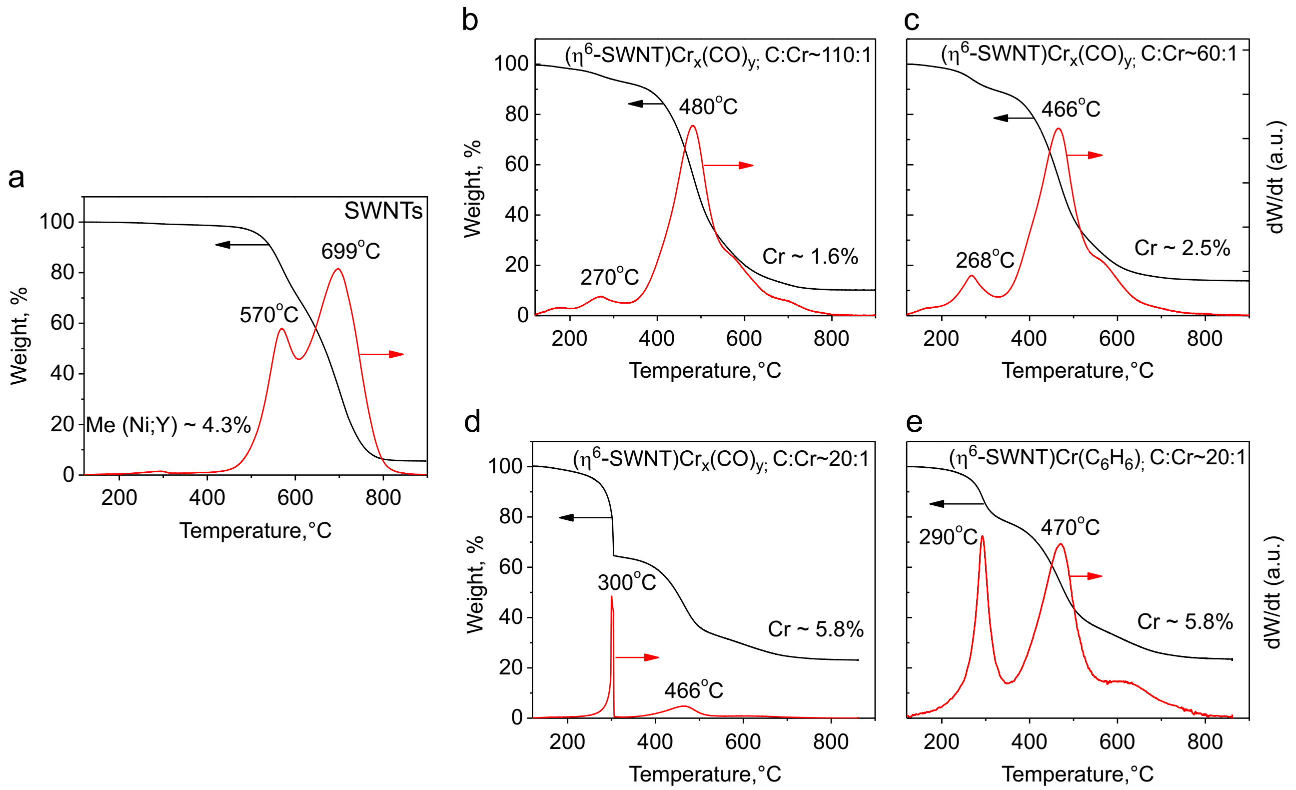


Fig. 1. TGA recorded in air at a heating rate of 5 °C/min: (a) purified SWNT starting material; (b) $(\eta^6\text{-SWNT})Cr_x(CO)_y$ synthesized by reacting SWNTs with $Cr(CO)_6$ for 1 day; (c) $(\eta^6\text{-SWNT})Cr_x(CO)_y$ synthesized by reacting SWNTs with $Cr(CO)_6$ for 3 days; (d) $(\eta^6\text{-SWNT})Cr_x(CO)_y$ synthesized by reacting SWNTs with $Cr(CO)_6$ for 5 days; and (e) $(\eta^6\text{-SWNT})Cr_x(C_6H_6)_y$ synthesized by reacting SWNTs with benzene $Cr(CO)_3$ for 5 days.

the presence of small chromium clusters: 1–2 nm in the case of (η^6-SWNT)Cr$_x$(CO)$_y$ obtained by a reaction for 1 day (Fig. 2b), and 2–4 nm for (η^6-SWNT)Cr$_x$(CO)$_y$ obtained by a reaction for 3 days (Fig. 2c). This is also confirmed by the dark field STEM images in Fig. 2d–f, in which the chromium clusters appear as bright particles.

We previously suggested the mechanism in eq. (1) of Scheme 1, for the cluster formation, where it may be seen that the graphene Clar structures template the condensation of the chromium clusters and facilitate the loss of carbon monoxide [16].

If we assume a bond length, $l = 1.42$ Å for graphene, then the Cr–Cr bond distance implied by the final structure in eq. (1) is about 2.46 Å, which is below the value of 2.8–3.0 Å found in small molecular clusters containing the Cr–Cr bond and chromium metal, but could probably be accommodated by a distortion of the ideal structure [19–22]. However the mechanism in eq. (1) requires a disruption of the periodicity of the graphene Clar structures and in eq. (2) we suggest an alternative mechanism, which does not interfere with the long range order of the Clar structures, but instead relies on bond rearrangements within the local structures. The last step in this reaction sequence does not formally satisfy the 18-electron rule, but it may be feasible given the electronic structure found in related compounds [23–26].

The size of the clusters remains about 2–4 nm when the reaction time is increased from 3 to 5 days (Fig. 3 a, b); thus in the complexation reaction of SWNTs with Cr(CO)$_6$, the increase of

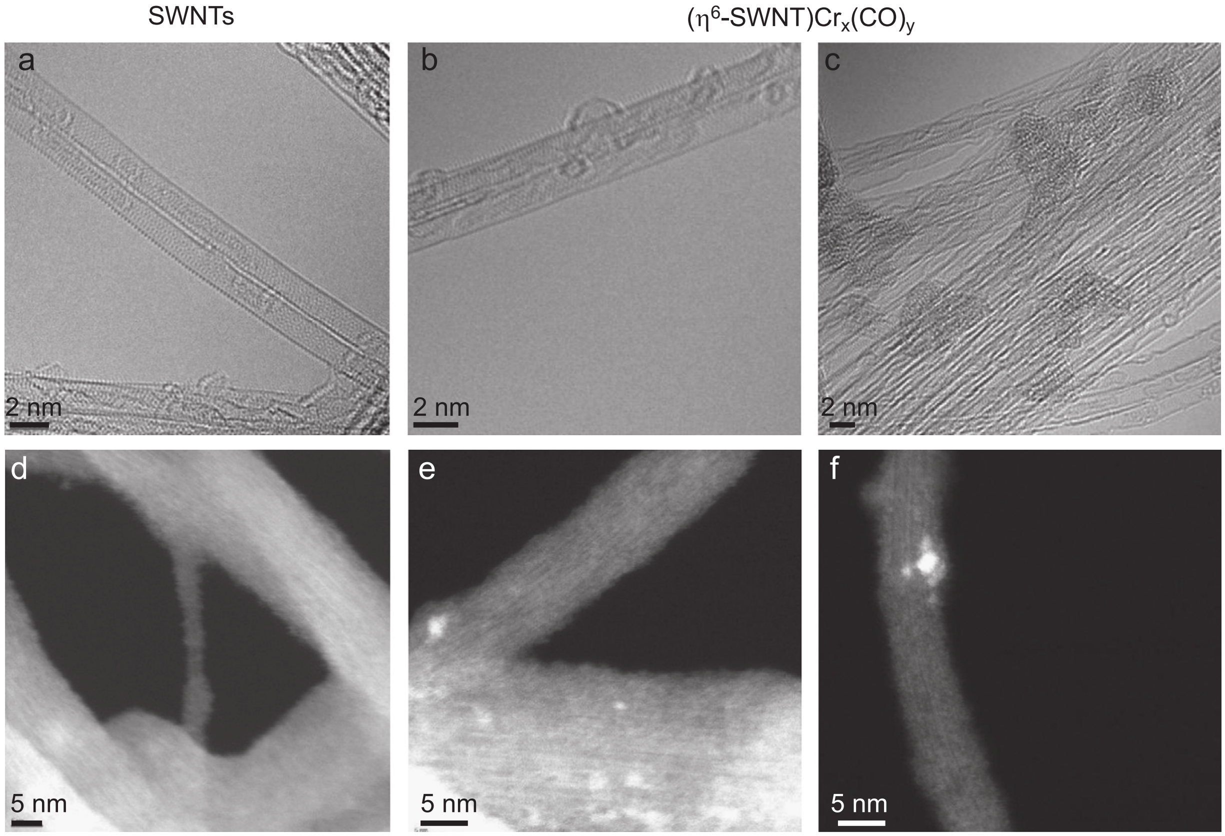
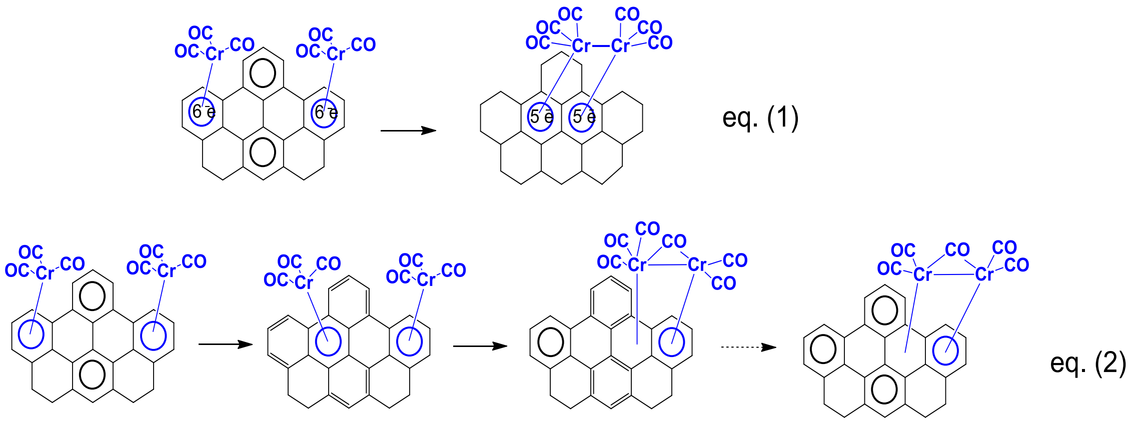


Fig. 2. HRTEM images of (a) purified SWNTs, and (b)–(c) Cr-functionalized SWNTs, (η^6-SWNT)Cr$_x$(CO)$_y$, synthesized by reaction of SWNTs with Cr(CO)$_6$ for 1 day (b) and 3 days (c). Annular dark filed images of the materials: (d) SWNTs, (e) (η^6-SWNT)Cr$_x$(CO)$_y$ synthesized by 1 day reaction and (f) (η^6-SWNT)Cr$_x$(CO)$_y$, synthesized by a 3-day complexation reaction.



Scheme 1. Proposed mechanisms of Cr-cluster formation on carbon nanotubes.

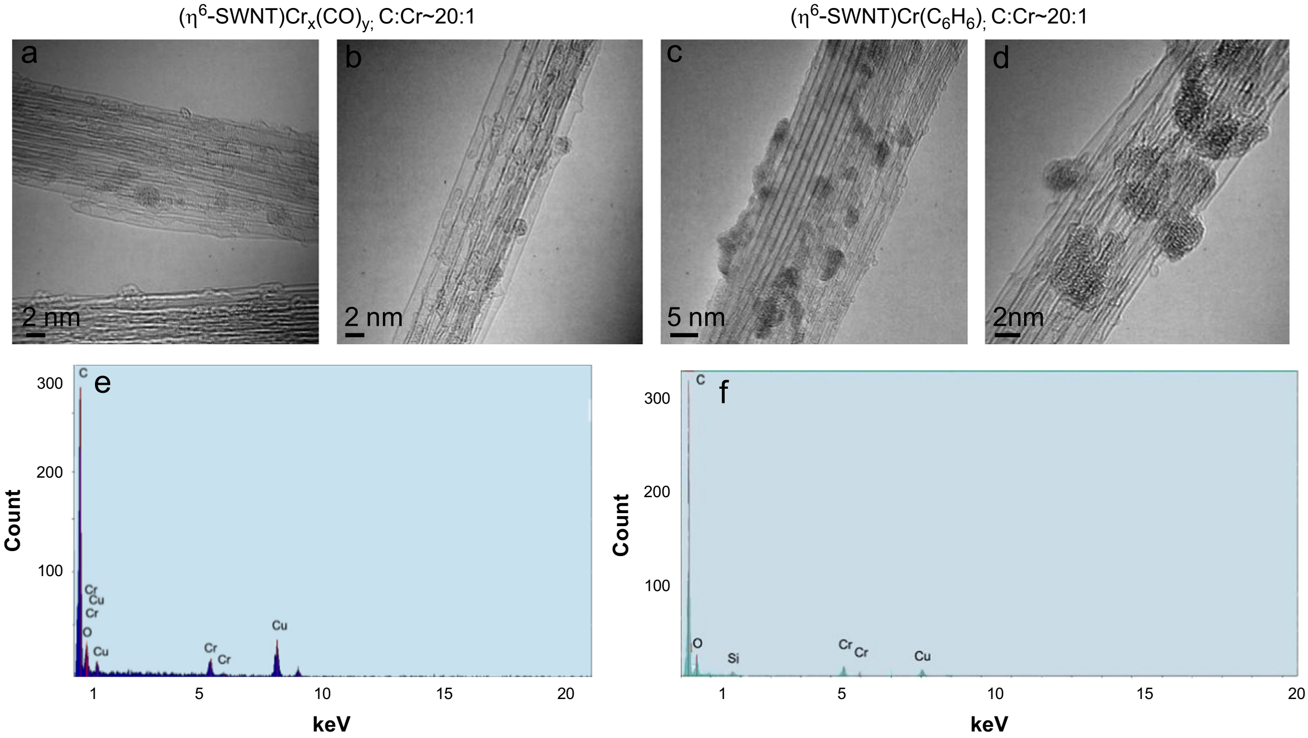


Fig. 3. TEM images of (a, b) Cr-functionalized SWNTs, (η^6-SWNT)$Cr_x(CO)_y$, synthesized by reaction of SWNTs with $Cr(CO)_6$ for 5 days, and (c, d) (η^6-SWNT)$Cr_x(C_6H_6)_y$, synthesized by reaction of SWNTs with (η^6-C_6H_6)$Cr(CO)_3$ for 5 days. (e, f) EDS measurement of (η^6-SWNT)$Cr_x(CO)_y$ and (η^6-SWNT)$Cr_x(C_6H_6)$ showing the presence of Cr.

reaction time leads to the formation of more metal clusters attached to the SWNT walls, but it does not affect significantly the cluster size.

Comparison with the Cr–SWNT material, prepared by reacting SWNTs with $BzCr(CO)_3$ for 5 days, shows that both materials contain similar metal clusters with a size of 2–4 nm and atomic C–Cr ratio of 20:1 (Fig. 3c, d).

The TEM analysis suggests that in both Cr–SWNT materials, the Cr-clusters are predominantly attached to the exterior walls of the SWNTs, although in the case of the $Cr(CO)_6$ precursor some of the Cr clusters appear to be in an endohedral configuration. The clusters are inhomogeneously distributed along the SWNTs, which may be associated with the high mobility of the Cr atoms on graphitic surfaces.

4. Conclusions

The solution phase synthesis of Cr-complexed SWNTs can lead to the formation of exohedral Cr-clusters attached to the SWNT walls. The size of the clusters depends on the duration of the complexation reaction and it is in the range from less than 1 nm to about 4 nm. We suggest that the carbon nanotube benzenoid structure templates the condensation of the chromium atoms and facilitates the loss of carbon monoxide leading to well defined clusters.

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