



Photochemical Generation of Bis-Hexahapto Chromium Interconnects Between the Graphene Surfaces of Single-Walled Carbon Nanotubes

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Conceptual insights

The building block of carbon nanotubes and graphene is the graphitic surface of sp_2 hybridized carbon atoms which are incorporated in continuous, periodic poly-benzenoid structures. Due to their high degree of perfection there is no simple way to covalently interconnect such structures without disrupting the electronic band structure and introducing sp_3 carbon atoms into the lattice. The introduction of rehybridized carbon atoms into these graphitic structures has been shown to decrease the electrical conductivity and the mobility of the carriers and to lead to localized structures. In this report we extend our use of the covalent organometallic hexahapto-bond in the conjugation of these delocalized graphene surfaces by exploring photochemical routes for the preparation of $(\text{Cr}(\text{SWNT}))_n$ junctions (SWNT = single-walled carbon nanotubes), in random networks of SWNT thin films. We show that standard organometallic chromium precursors may be utilized to improve the conductivity of metallic, semiconducting, and non-separated SWNT thin films by the use of simple photochemical reactions utilizing the appropriate wave-length of light. The work supports the idea that the minimal rehybridization which is implicit in the formation of organometallic hexahapto-linkages to conjugated graphene surfaces is the only form of covalent bonding which is capable increasing the conductivity of these networks.

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The electrical conductivity of single-walled carbon nanotube (SWNT) networks is strongly enhanced by the high vacuum ebeam deposition of transition metals. In the present communication we demonstrate that it is possible to accomplish the same chemical functionalization reactions at room temperature beginning with simple organometallic precursors. We show that the photochemically induced reactions of solutions of $\text{Cr}(\text{CO})_6$, $\text{Cr}(\eta^6\text{-benzene})(\text{CO})_3$, and $\text{Cr}(\eta^6\text{-benzene})_2$ with thin films of semiconducting, metallic and non-separated SWNT films all lead to strongly enhanced conductivities which produce consistent results for each SWNT type among the three organometallic reagents. We conclude that all three of these reactions lead to the generation of covalent $(\eta^6\text{-SWNT})\text{Cr}(\eta^6\text{-SWNT})$ interconnects which provide conducting pathways in the SWNT films and our results broaden the applicability of the transition metal bis-hexahapto-bond as an electronically conjugating linkage between graphene surfaces.

Introduction

The electrical interconnection of the graphene surfaces of carbon nanomaterials remains a challenging problem in carbon electronics^{1,2} and it is now well known that chemical functionalization processes in which the conjugated carbon atoms are fully pyramidalized to the geometry required for sp^3 hybridization, lead to a loss of conductivity and mobility in these systems.³ However the formation of hexahapto-organometallic bonds to the graphene surface largely preserves the electronic structure of these polybenzenoid carbon structures,⁴⁻⁸ and the deposition of chromium atoms on thin films of SWNTs exerts a dramatic effect on the percolation threshold of SWNT networks which we have attributed to the formation of organometallic bonds of the form $\text{Cr}(\eta^6\text{-SWNT})_2$.⁹

The preparation of hexahapto-bis(arene) metal complexes may be accomplished by a number of different routes, but only two have found general application:¹⁰ the metal vapor synthesis (MVS) technique of Timms¹¹ and the solution-based Fischer-Hafner process.¹² The preparation of hexahapto-arene-chromium-tricarbonyls can be accomplished by the solution reaction of $\text{Cr}(\text{CO})_6$ with the appropriate arene under thermal or photochemical conditions,^{13, 14} although neither process proceeds to the fully substituted $\text{Cr}(\eta^6\text{-arene})_2$ complexes.¹⁵ We have found that variants of some of these gas phase MVS and solution-based thermal reactions

are capable of realizing the organometallic functionalization of extended, periodic π -electrons systems such as single-walled carbon nanotubes (SWNT) and graphene.^{8, 9, 16-18} The MVS reactions are accomplished within the high vacuum chamber of an ebeam evaporation system and this has allowed us to show that the formation of these hexahapto-bis($\eta^6\text{-SWNT}$) metal complexes dramatically increases the conductivity of thin films of SWNTs.

In the present communication we introduce facile solution-based routes for the ambient temperature introduction of organometallic atomic interconnects between the graphene surfaces of SWNTs which obviate the need for high vacuum reaction vessels. We show that photochemical reactions of reagents such as $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\eta^6\text{-benzene})(\text{CO})_3$ are very effective in forming $\text{Cr}(\eta^6\text{-SWNT})_2$ complexes which act as interconnects between the graphitic surfaces, as evidenced by an abrupt increase in conductivity on irradiation of thin films of these materials in the presence of the appropriate reagents. Surprisingly we find that room temperature treatment of the SWNT films with solutions of $\text{Cr}(\eta^6\text{-benzene})_2$ spontaneously produces the same effect apparently as a result of incidental exposure to room light.

Experimental

Nanotube sample preparation

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The single-walled carbon nanotube thin films were prepared by vacuum filtration using aqueous suspensions of semiconducting (SC, Nanointegris Inc. - IsoNanotubes-S 99%), metallic (MT, Nanointegris Inc. - IsoNanotubes-M 99%) and non-separated purified nanotubes (NS, Nanointegris Inc. - PureTubes). The volume of suspension for vacuum filtration using a mixed cellulose ester membrane (Millipore VCWP), was calculated on the basis of the concentration of the SWNT dispersion and the measured film density so as to obtain a film of thickness, $t = 8$ nm.¹⁹ The SWNT film and filter membrane was cut into 6mm x 2mm pieces and the SWNT film was transferred onto a glass substrate with pre-patterned gold electrodes (Figure 2) using a hot acetone vapor process described in the literature.²⁰ The films for the conductivity experiments were measured under a microscope in order to determine the film geometry for the final film conductivity calculation. The samples were vacuum annealed (8h at 300°C, 10⁻⁶ torr), immediately before use in order to remove atmospheric dopants and transferred into a glove box (O₂, H₂O < 1ppm) without further air exposure.

Reaction conditions

Approximately 1×10^{-3} M solutions of the chromium compounds (Cr(CO)₆ - 3.5 mg, Aldrich 98%, Cr(η⁶-C₆H₆)(CO)₃ - 2.4 mg, Aldrich 98%, Cr(η⁶-C₆H₆)₂ - 2 mg, Strem 97%) were prepared in degassed acetonitrile (10 ml, Aldrich anhydrous, 99.7%); the samples were dipped into the reagent solutions and irradiated inside the glove box. The light sources for the photochemistry consisted of a handheld dual UV source (Spectroline ENF-260C), making use of the UVC (254nm) light in the case of Cr(CO)₆ and UVA (365nm) light for the Cr(η⁶-C₆H₆)(CO)₃ samples, whereas for the Cr(η⁶-C₆H₆)₂ experiments the ambient room light was sufficient.

Characterization

The resistance of the samples was measured using a Keithley 2400 Source Meter unit driven with custom LabVIEW software with sample contacts made via feed throughs into the glove box. The UV-VIS spectroscopy of the solutions was performed with a CARY 5000 grating spectrometer using 1mm quartz cuvettes.

Results and Discussion

The experiments we describe are most closely related to our MVS conductivity studies which were conducted in a Temescal BJD 1800 cryo-pumped high vacuum ebeam evaporator that allows the exposure of appropriately wired SWNT thin films to a flux of metal vapors.^{9, 18, 19, 21} We initially transferred this experiment to a 1" pyrex tube which was maintained under an argon atmosphere and was therefore amenable to heating in a tube furnace or irradiation by an external light source (in these studies we used a handheld UV lamp). However when we discovered the room temperature photochemical routes we were able to carry out the experiments in a glove box which allowed the whole process to be conducted under inert atmosphere conditions, including the treatment of the films with the organometallic reagents. The absorption spectra of these reagents in acetonitrile solution are shown in Figure 1 together with the wavelength of light which was found to be successful in inducing the photochemical reactions.

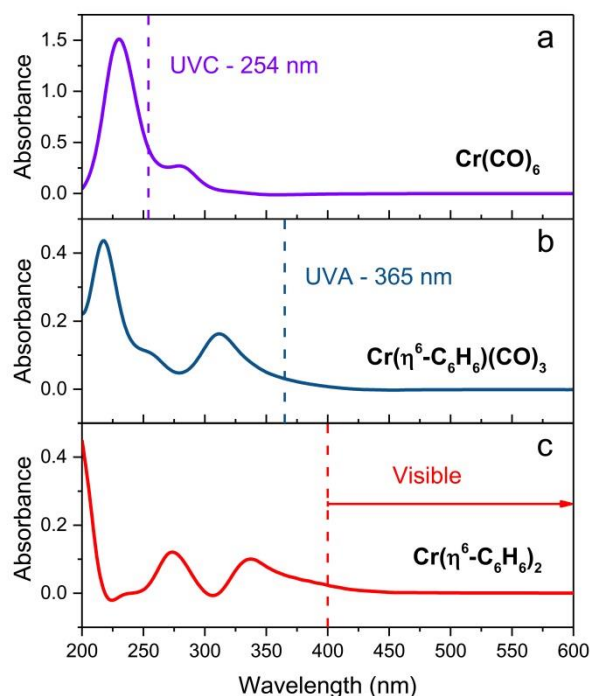


Figure 1. UV-VIS spectra of the chromium reagents dissolved in acetonitrile and the wavelengths of light used in the photochemical experiments. a) Cr(CO)₆ showed reaction upon irradiation with 254 nm wavelength UVC light. b) Cr(η⁶-benzene)(CO)₃ reacted in the presence of 365 nm wavelength UVA light. c) Cr(η⁶-benzene)₂, dashed line and arrow indicates the wavelength range used in the reaction of this compound.

Typically we first measured the pristine film conductivities on overnight annealing under argon in order to remove residual solvent and atmospheric contaminants and to provide a baseline for the organometallic reactions. The protocol for the experiments is shown in Figure 2 and consists of the exposure of a suitably wired SWNT thin film (thickness, $t = 8$ nm), to a solution of the organometallic precursor by dipping the film in an acetonitrile solution of the reagent (concentration $\approx 1 \times 10^{-3}$ M) in a glove box followed by the measurement of the conductivity of the SWNT thin film at ambient temperature. For these experiments we included three types of SWNT thin films, as described in the experimental section: semiconducting (SC-), metallic (MT-), and non-separated (NS-) SWNTs; the transport properties of these films have been previously characterized in connection with our MVS experiments.^{9, 22} The conductivities of the pristine films are sensitive to atmospheric doping (particularly SC-SWNTs), but representative room temperature conductivities of the annealed films are as follows: $\sigma \approx 3$ S/cm (SC-SWNT), 350 (MT-SWNT), 300 (NS-SWNT).

The irradiation of matrices containing Cr(CO)₆ with UV light is known to lead to the successive dissociation of the CO ligands which are replaced with molecules from the surrounding matrix;^{23, 24} the high reactivity of these intermediates leads to complexation with inert ligands such as acetonitrile,²⁵ alkanes,²⁶ dihydrogen,²⁷ and inert gases (Ne, Ar, Kr, Xe).^{23, 24}

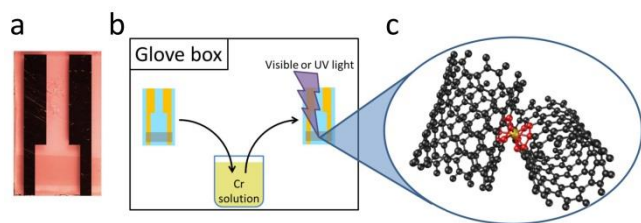
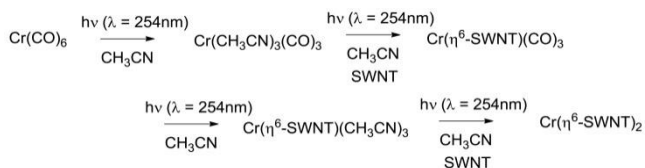


Figure 2. Schematics of the photochemical reaction procedure: a) microscope image of a representative sample, where the conducting channel is of dimensions: length, $l = 4$ mm, width, $w = 2$ mm, and thickness, $t = 8$ nm. b) After overnight annealing samples were transferred into a glove box and electrically connected for resistance measurement. While continuously monitoring the resistance, the samples were dipped into solutions of the chromium reagent and irradiated with visible or UV light. c) All reagents lead to the formation of $\text{Cr}(\eta^6\text{-SWNT})_2$ complexes at the SWNT junctions.

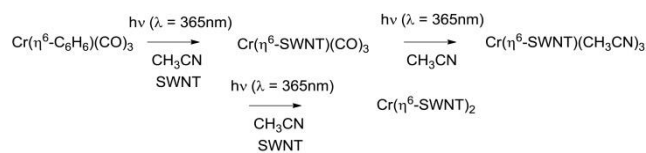
We found that SWNT films in the presence of $\text{Cr}(\text{CO})_6$, in which the solvent had been removed by evaporation, did not experience a discernible change in conductivity on irradiation and thus we conclude that acetonitrile complexes²⁵ such as $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ must be implicated in these reactions and we have previously shown that this complex reacts readily with exfoliated graphene samples to give $(\eta^6\text{-graphene})\text{Cr}(\text{CO})_3$.⁷ The subsequent reactions with $\text{Cr}(\text{CO})_6$ were conducted without removal of the acetonitrile and we postulate the following reaction pathway (Scheme 1).



Scheme 1. Reaction scheme for $\text{Cr}(\text{CO})_6$.

As may be seen in Figure 3a, the response of the conductivity is essentially complete in the first 25 s of UVC irradiation ($\lambda = 254$ nm) and we were unable to detect differences in the reactivity of the three SWNT films toward the species generated from the photolysis of $\text{Cr}(\text{CO})_6$; the use of UVA light ($\lambda = 365$ nm) produced no discernible change in the film conductivities. The changes in conductivity are discussed in detail later, but they show the same qualitative behavior as was found previously in the MVS experiments,⁹ with the SC-SWNT films experiencing the strongest enhancement of the conductivity (by a factor of more than two orders of magnitude in the present experiments).

We found that SWNT films previously exposed to an acetonitrile solution of $\text{Cr}(\eta^6\text{-benzene})(\text{CO})_3$ when irradiated with UVA light ($\lambda = 365$ nm) led to a virtually identical set of conductivity responses (Figure 3b), although on a slightly shorter time scale and in this case the use of UVC light ($\lambda = 254$ nm) produced no discernible effect on the film conductivities. The photochemistry of $\text{Cr}(\eta^6\text{-benzene})(\text{CO})_3$ is known to be complex,^{26, 28} but based on the wave length of the light found to initiate reaction, we postulate the following reaction mechanism (Scheme 2), as $\text{Cr}(\eta^6\text{-benzene})(\text{CO})_3$ is known to undergo both arene exchange and CO loss under irradiation with light.²⁹



Scheme 2. Reaction scheme for $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_3$.

The exposure of the SWNT films to a solution of $\text{Cr}(\eta^6\text{-benzene})_2$ in acetonitrile in the presence of room light (filtered through the plexiglass of the glove box), lead to immediate reaction as evidenced by the instantaneous response of the conductivity (Figure 3c).

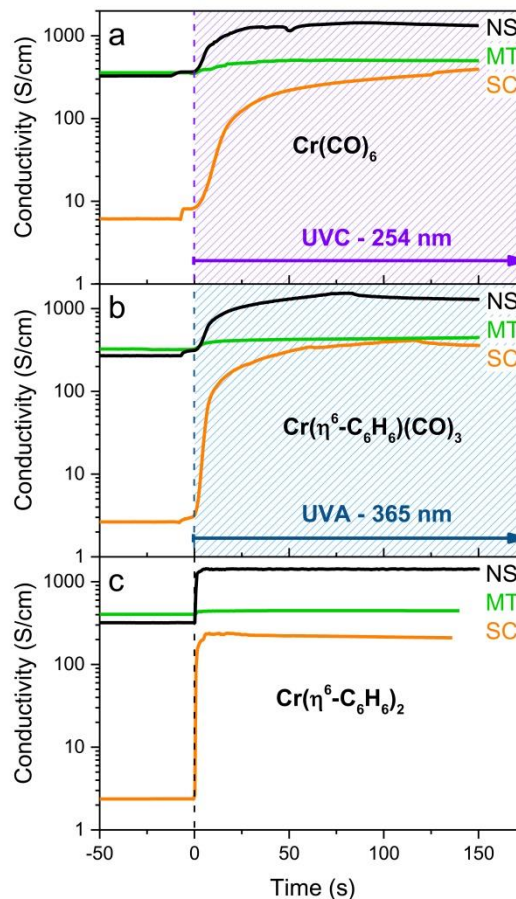


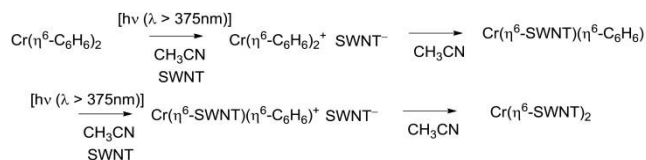
Figure 3. Evolution of SWNT thin film conductivities on photochemical reaction with the chromium reagents, as a function of SWNT type: semiconducting (SC-), metallic (MT-) and nonseparated (NS-) SWNTs. a) $\text{Cr}(\text{CO})_6$, after dipping the samples in the solution, 254 nm wavelength UVC light was used to initiate the reaction at time = 0 s (dashed line). b) $\text{Cr}(\eta^6\text{-benzene})(\text{CO})_3$, after irradiation with 365 nm wavelength UVA light was used to initiate the reaction at time = 0 s (dashed line). c) $\text{Cr}(\eta^6\text{-benzene})_2$, after dipping the samples into the solution at time = 0 s (dashed line), in the presence of room light.

The benzene ring is usually regarded as kinetically inert toward arene exchange reactions in $\text{Cr}(\eta^6\text{-benzene})_2$ and benzene is noted for its ability to replace other arenes under appropriate conditions.^{10, 25, 30, 31} Furthermore $\text{Cr}(\eta^6\text{-benzene})_2$ is known to be quite stable to irradiation and it does not normally undergo light-induced arene exchange.²⁹ However, based on the redox potentials of $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$ (reduction potential of $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2^+$, $E_{1/2} = -0.69$ V against SCE in DME)¹⁵ and SC-SWNTs (reduction potential of electric arc SWNTs, $E_{1/2} \approx -0.5$ V against

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SCE in DMSO),³² it seems likely that the reaction may proceed by a series of electron transfer processes as the metallocene cations generally undergo facile arene exchange reactions.^{10, 31}

In Scheme 3 we show the reaction as a photochemical process which requires visible light for its initiation, but as may be seen in Figure 4 it seems the reaction is able to proceed in the absence of light, but at a much slower rate in accord with the redox potentials discussed above which are thermodynamically sufficient for spontaneous electron transfer (Scheme 3).



Scheme 3. Reaction scheme for $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$.

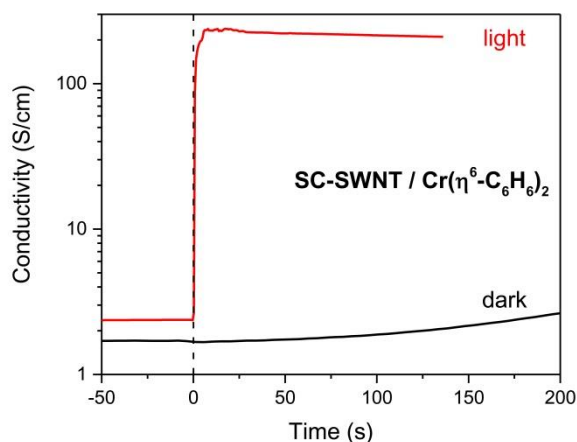


Figure 4. Evolution of the conductivity of semiconducting (SC-) SWNT films after dipping in $\text{Cr}(\eta^6\text{-benzene})_2$ solution, in the presence of room light and in the dark.

It is apparent from Figure 3 that the photochemical reactions of all three organometallic species lead to the same modification of the electronic structure of the SWNT films and the final conductivities show good agreement after chromium functionalization: $\sigma \approx 300$ S/cm (SC-SWNT), 500 S/cm (MT-SWNT), 1250 S/cm (NS-SWNT), which gives the following conductivity enhancements: $(\sigma - \sigma_0) / \sigma_0 \approx 100$ (SC-SWNT), 1 (MT-SWNT), 4 (NS-SWNT), where σ is SWNT film conductivity after functionalization and σ_0 is conductivity of the pristine SWNT film. These values exceed the previously determined MVS results which gave values of: $(\sigma - \sigma_0) / \sigma_0 \approx 70$ (SC-SWNT) and 0.6 (MT-SWNT), for films of thickness, $t = 8$ nm.⁹ We assign the slightly improved conductivities of the solution processed films to the ability of the solvent to penetrate and uniformly disperse the reagents throughout the films thereby allowing contact with SWNT junctions within the film that are not accessible to the line-of-sight flux of metal atoms that is characteristic of high vacuum evaporation processes. For films of thickness, $t = 2$ nm the MVS experiments gave values of $(\sigma - \sigma_0) / \sigma_0 \approx 130$ (SC-SWNT) and 0.8 (MT-SWNT).⁹ Previous experiments show that the stoichiometry of Cr atoms necessary to bring about these conductivity enhancements is very low.^{19, 21}

As noted above, the reaction rates estimated from the conductivities, suggest the following order of reagent reactivities under the specified conditions: $\text{Cr}(\eta^6\text{-benzene})_2 > \text{Cr}(\eta^6\text{-benzene})(\text{CO})_3 > \text{Cr}(\text{CO})_6$, whereas under most circumstances the reverse order might be expected in reactions of these reagents with free arenes.^{10, 15} Nevertheless the high reactivities shown in Figure 3 are in accord with our frontier molecular orbital theory (FMO) analysis of the electronic structure of graphene, in which the high lying HOMOs and low lying LUMOs together with the presence of appropriate FMOs suggests that graphene and related small band gap nanomaterials such as SWNTs might be very reactive in certain circumstances, including organometallic functionalization chemistry.^{8, 33}

The conductivity enhancements of the MT-SWNTs are less than in the case of the SC-SWNTs which may be related to the different symmetries of the FMOs in the case of arm chair and semiconducting SWNTs which will affect the interaction with the transition metal d-orbitals;³⁴ furthermore two-terminal conductances measured across MT-MT junctions of pristine SWNTs are comparable to the two-terminal conductances of the individual SWNTs.³⁵

Conclusions

In conclusion, we have discovered a series of facile routes for the photochemical solution-based, ambient temperature introduction of transition metal interconnects between the surfaces of semiconducting, metallic and non-separated single-walled carbon nanotubes (SWNT)s that substantially increase the conductivity of thin SWNT networks. We show that the reagents exhibit the following order of reactivities $\text{Cr}(\eta^6\text{-benzene})_2 > \text{Cr}(\eta^6\text{-benzene})(\text{CO})_3 > \text{Cr}(\text{CO})_6$ toward the SWNT networks based on the conductivity responses, although all reagents lead to the same final conductivities and involve the $\text{Cr}(\eta^6\text{-SWNT})_2$ linkages as the common feature. The broad scope of these organometallic reactions suggest that the present work will allow the preparation of the full complement of organometallic complexes of any carbon-based nanomaterial containing the poly-benzenoid electronic structure, particularly SWNTs and graphene structures thereby allowing the further development of atomtronics.¹⁷

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Notes and references

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The linkage of single-walled carbon nanotube junctions by the photochemistry of organometallic chromium reagents produces dramatic increases in network conductivity.

