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Effect of Group 6 Transition Metal Coordination on the Conductivity of Graphite Nanoplatelets

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ABSTRACT

Graphite nanoplatelets (GNPs) were reacted with transition metal (M) carbonyls followed by annealing and compaction to remove the CO ligands and form bis-hexahapto bonds between the GNP surfaces. The M-GNP films (M = Cr, W, Mo) were characterized with Raman spectroscopy and conductivity measurements. It was observed that interconnection of the graphitic faces of GNPs by bis-hexahapto metal coordination resulted in a decrease of electrical conductivity. The complexes offer promise as catalysts and in the fabrication of new 3-D electronic materials.

1. Introduction

Coordination complexes of transition metals with graphitic materials are of interest from the standpoint of their application as conjugated organometallic catalysts [1–3], as electronic and magnetic materials [4–8], and have been widely studied by theoretical models [9]. The transition metal chemistry of polycyclic aromatic hydrocarbons (PAHs), where the PAHs acted as arene ligands, continues to attract attention in organometallic chemistry [10–12].

Metal–arene oligomeric complexes are generally synthesized by condensation of metal vapors with neat arene ligands [4], although solution-phase synthetic methodologies have also been reported [5,6]. Recently we reported a series of organometallic complexes of graphene, and single-walled carbon nanotubes (SWNTs), where the graphene sheet or the SWNT side-wall act as the primary ligand, using both solution-phase and metal atom vapor synthetic techniques [3,13,14]. In the present manuscript we report the preparation of bulk graphitic–transition metal complexes by the solution processing of graphite nanoplatelets (GNPs) [15,16], in the presence of transition metal (M) carbonyls, where M = Cr, Mo, W.

2. Experimental

2.1. Materials

Natural graphite (NG, average flake size = 300 μm) was obtained from TIMCAL Graphite and Carbon. Dibutyl ether, anhydrous tetrahydrofuran (THF), chromium hexacarbonyl, molybdenum hexacarbonyl, and tungsten hexacarbonyl were obtained from Sigma-Aldrich.

2.2. Preparation of graphite nanoplatelets (GNP)

The GNPs were prepared by acid intercalation (H_2SO_4/HNO_3, 3:1; 15 h, room temperature), followed by thermal shock exfoliation; the resulting material consists of incompletely exfoliated graphene sheets, in which there is a broad distribution of particle sizes [15,16]. The exfoliated material (1 g) was dispersed in dibutyl ether (400 mL Bu_2O) by shear mixing for 30 min followed by bath sonication for 24 h to obtain the final GNP suspension (~2.5 mg/mL). UV–vis spectra of the diluted suspensions were collected in order to confirm the concentration of the suspension (by reference to the graphitic molar extinction coefficient, $\varepsilon_{550nm} = 500\ L\ mol^{-1}\ cm^{-1}$) [17,18].

2.3. Synthesis of metal coordination complexes

In a typical experiment, a mixture of the GNP/Bu_2O suspension (20 mL, 50 mg, 4.17 mmol carbon, 500 equivalents) and tetrahydrofuran (2 mL THF) was degassed with argon for 1 h and the metal carbonyl (0.008 mmol, 1 equivalent) was added [3,14]. The resulting

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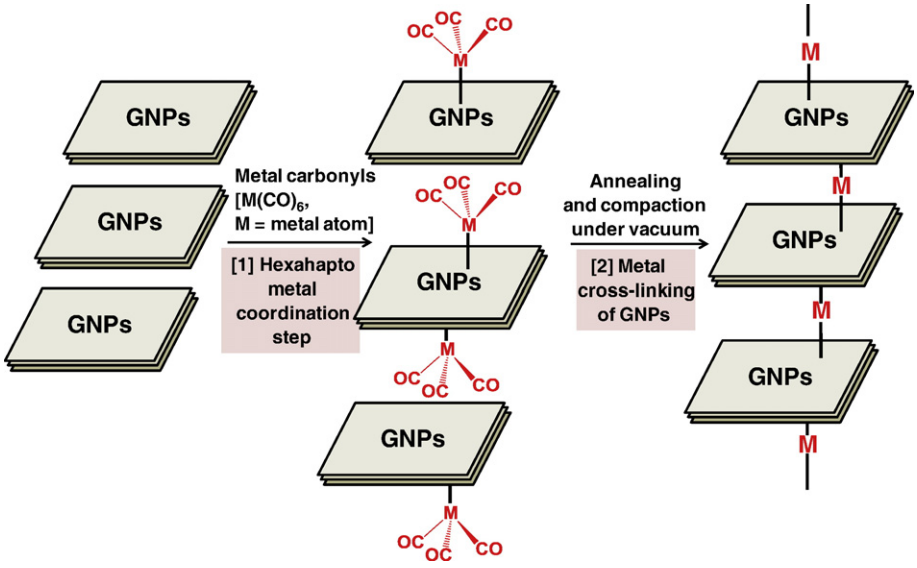

Scheme 1. Preparation of metal–GNPs complexes: (1) reaction of GNPs surfaces with metal carbonyls, (2) annealing and compaction to cross-link the GNPs.

mixture was refluxed at 140 °C under argon for 24 h, allowed to cool to room temperature, and then filtered. Thin films of the M-GNP complexes of pre-determined diameter and thickness were fabricated by vacuum filtration (Durapore 0.1 μm VVPP membrane filter) of a known volume of the GNP suspension in dibutylether (GNP/Bu_2O).

2.4. Preparation of annealed and compacted M-GNP films

In a typical experiment, the M-GNP films were pressed in a stainless steel cell, in which the pole faces of the die were covered with Teflon films. The cell was connected to a vacuum system, which included a liquid nitrogen trap and evacuated to a pressure of 10^{-4} Torr and a pressure of 500 lb applied to the plunger. The temperature was slowly increased to 100 °C by heating the plates of the hydraulic press and held at this temperature for 2 h. Then the pressure was increased to 1000 lb and a temperature of 200 °C was applied to the film for 4 h, after which the apparatus was allowed to cool to room temperature, the vacuum released and the M-GNP film (thickness, $t \sim 200$ μm) was removed from the die for characterization.

2.5. Raman spectroscopy

Raman spectral data were acquired with a Nicolet Almega XR Dispersive Raman microscope with a 0.7 μm spot size and 532 nm laser excitation. The laser power was reduced to 2.5 mW to prevent damage to the sample and the spectra were taken with 10 s acquisition time.

2.6. Conductivity

The M-GNP film was diced to give a specimen size of ~1 mm (w) × ~2.5 mm (l), the sample contacted with silver paint and the conductivity measured over the temperature range 90–350 K using a Keithley 236 4-point Source-Measure Unit in conjunction with a Keithley 2700 Unit for the temperature measurement.

3. Results and discussion

3.1. Synthesis

In our previous work we reacted $Cr(CO)_6$ and (η^6-benzene)$Cr(CO)_3$ with various forms of graphene [exfoliated graphene (XG), epitaxial graphene (EG), and highly oriented pyrolytic graphite (HOPG)], with surface functionalization as the primary goal [3]. Thus we prepared mono-hexahapto (η^6-graphene)$Cr(CO)_3$ and (η^6-graphene)Cr(η^6-benzene) structures from all of the graphene starting materials, but in the reaction with XG we also observed the formation of bis-hexahapto (η^6-graphene)Cr(η^6-graphene).

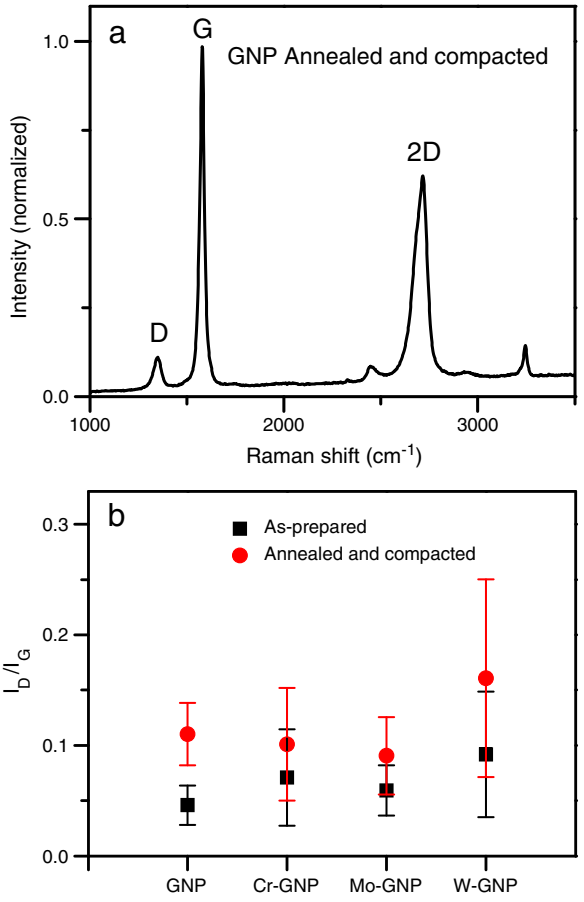

Fig. 1. (a) Raman spectrum of annealed and compacted GNP starting material. (b) I_D/I_G ratio in the Raman spectra of the samples before and after annealing and compaction; error bar represents statistics between measurements at different locations.