Encapsulation of cobalt phthalocyanine molecules in carbon nanotubes

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Abstract. We report on the encapsulation of cobalt phthalocyanine (CoPc) molecules in double and multi-walled carbon nanotubes. Transmission electron microscopy imaging confirms the filling and shows pristine outer walls after cleaning. We also discuss Co 2p photoemission results, which reveal that hybridization interaction with the surrounding nanotube is likely, resulting in a peak attributed to Co(III).

Phthalocyanines are a class of stable, blue-green organic pigments which can be synthesized with a variety of metal ions at their centre. They are related to molecules like heme and chlorophyll, and likewise show useful optical properties. We have focussed our experiments on cobalt phthalocyanine (CoPc) where the Co ion is in a nominal 3d\textsuperscript{7} configuration and the surrounding, planar ligand field of the phthalocyanine molecule lifts the degeneracy of the d-orbitals such that the 3d\textsubscript{3z^2-r^2} orbital is singly occupied resulting in total electron spin S=1/2 (the 3d\textsubscript{x^2-y^2} orbital is empty). This orbital is oriented perpendicular to the plane of the molecule, and hence when stacked, neighbouring molecules can interact via the dipole-dipole mechanism and form spin-singlets, which means that bulk CoPc is a paramagnet [1]. However, electron doping (A\textsubscript{x}CoPc, with A alkaline metals and x \geq 1) is reported to first complete the 3z\textsuperscript{2}-r\textsuperscript{2} filling before subsequently filling up a π-orbital, where electrons can align parallel, and so regain magnetism [2]. In contrast, in transition metal (TM)-phthalocyanines where the d-level is less than half-filled, such as Mn(II)Pc, a negative trend of the Curie temperature with doping has been observed [3]. Analogous to intercalated fullerene compounds, insulator-metal transitions have recently been reported in potassium doped TM-Pc’s [4]. With this in mind, restricting phthaolocyanine assemblies to one or two dimensions raises a variety of possibilities as to what will happen to the CoPc electronic structure. Especially when this is realized through incarceration in carbon nanotubes, which not only provide the containment, but can also act as an electron donating or accepting reservoir [5].

Separate batches of catalyst-free, purified double walled (DWNT) and multi-walled carbon nanotubes (MWNTs) were first oxidized in air at 360°C for 30 minutes followed by 375°C for 10 minutes to clean and open the tubes. They were then mixed with excess CoPc, sealed in a...
quartz tube at a vacuum of $10^{-6}$ torr, and heated at 370°C for up to 3 days. We found that CoPc that had settled on the outside of the tubes could be removed by repeated rinsing with a mixture of chloroform and 1% trifluoroacetic acid, as confirmed by Transmission Electron Microscopy (TEM) measurements which were performed in a JEOL4000EX LaB6 microscope. Resulting images of the DWNTs (containing a small percentage of triple walled tubes) are shown in Figure 1. Although the tubes are clearly filled, in contrast with, for instance, C$_{60}$ [6] and PTCDA [7] no clear ordering of the encapsulated molecules is observed in TEM. The intense electron beam used in TEM could, however, disturb or even damage the CoPc molecules whilst imaging [8]. Multi-walled tubes showed a larger degree of filling and were subsequently used for spectroscopy measurements (see also Ref. [9]).

In order to assess whether the molecules are damaged during encapsulation photoemission (PES) and near edge x-ray absorption fine structure (NEXAFS) measurements were performed at beamline I311 in MAXlab Lund, Sweden. The NEXAFS photon energies were calibrated using second order light, whereas PES measurements used the Fermi edge of the Ta sample clamp. Samples were made by drop-casting a suspension of CoPc@MWNT in methanol onto a silicon substrate. For comparison, measurements performed on an in-situ deposited sub-monolayer and bulk film of CoPc on a Ag(111) single crystal at beamline D1011 of MAX-lab are also shown.

Fig. 2 clearly shows that the molecules have survived intact, as the NEXAFS signatures of the encapsulated CoPc molecules compare well to those of bulk CoPc shown in the same figure. No angular dependence was observed in the NEXAFS of the nanotube sample and this was corroborated by scanning electron microscopy imaging (not shown) which showed a 3D disordered arrangement of nanotubes. This is in contrast to samples where nanotubes had aggregated together in large bundles in the suspension, which then adhered predominantly parallel (2D) to the substrate surface [9].

Cobalt 2p core level photoemission results, however, show an intriguing split structure for the Co 2p$_{3/2}$ peak, which is not seen in bulk CoPc films. A Gaussian fit to the spectrum, after subtraction of a polynomial background is shown in Fig. 3 and reveals the conventional Co(II) 2p$_{3/2}$ peak located at 780.7 eV plus its weak satellite at 788.2 eV [10]. Experiments on Co$_3$O$_4$, which holds both Co(II) and Co(III) species, place the binding energy of Co(III) around one eV below that of Co(II) as it is accompanied by changes in total spin and ligand field surroundings [11, 10]. We therefore also attribute the peak at 779.1 eV to a percentage of nominally Co$^{3+}$
ions. This means that we assume net electronic charge has been donated to the nanotube. We do keep in mind, however, that the precise coordination and hybridization interaction of the CoPc with the inner walls of the MWNT needs to be further investigated. The assignment of this peak being due to a Co(III) species is further confirmed by comparisons to spectra taken from bulk (thick multilayer) CoPc and a sub-monolayer of CoPc, both on an Ag(111) substrate, depicted in Fig. 4. For the thick film, only the 780.7 eV peak is seen, indicative of a pure, low spin Co(II) state. For the sub-monolayer film, an extra peak at 778.4 eV is observed, similar to that seen in monolayer films of related tetraaryl-porphyrins on Ag(111) reported by Lukaszyk et al., and is attributed to net electron donation from the Ag surface in the initial state, with a peak located just above the binding energy (778.1 eV) for metallic cobalt [12].

The last peak to discuss is located at 782.1 eV in the CoPc@MWNT and sub-monolayer, and 782.3 eV in the multilayer film. A peak at this position is consistent with individually unresolved contributions from multiplet splitting within the open d-electron shell [12], with the change in width following the value of the nominal oxidation state of the cobalt: being widest for the Co(III) and Co(II) mixture inside nanotubes to most narrow for the electron doped - less than Co(II) - sub-monolayer. We should, however, not neglect the possibility of radiation damage as observed in, for instance, SnPc [13] and cobalt salts [14]. For the Co(III) salt this resulted in an increased intensity of a satellite peak at 5 eV above the main line, whereas the Sn peak displayed an extra component at 1 eV above the original binding energy. At beamline I311 the power density at a photon energy of 1000 eV is of the order of several 10s Wm$^{-2}$, and long exposure ($\approx$2 hrs) was necessary to obtain the outline of the weak Co 2p spectrum of CoPc@MWNT. Although we do not want to rule out radiation damage completely, quick nitrogen core level spectra (10 min) at the same photon energy, obtained before and after the long Co 2p PES measurement showed no appreciable change in width or shape.

In conclusion, we have reported the encapsulation of CoPc molecules inside carbon nanotubes, as confirmed by TEM. Also, Co 2p PES indicates hybridization interaction with the surrounding nanotube seems to take place, and this will form the topic of future experiments.

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Figure 3. Co 2p core level spectrum of CoPc molecules encapsulated in multi-walled carbon nanotubes (CoPc@MWNT) taken at $h\nu = 1000$ eV. Also shown is a Gaussian peak fit to the spectrum, as well as the subtraction of a polynomial background. Top panel: fit residual.

Figure 4. Comparison of Co 2p core levels for a sub-monolayer (sub-ML) film of CoPc, CoPc@MWNT, and bulk CoPc, plus Gaussian peak fits (dash-dot) and Shirley background (dash) to the latter.

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