Analysing carbon based hybrid nanocomposites displaying interfacial phenomena with scanning transmission electron microscopy and related techniques

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Hybrid materials where organic and inorganic constituents are combined, have gained popularity. In the literature, carbon based allotropes such as graphene and carbon nanotubes have been combined with metal or metal oxide nanostructures. Such nanomaterials present not only properties of the individual constituents but also new properties originating from defects at the interface between them. Therefore, understanding the nanostructure and chemical properties along with the coverage of the inorganic constituents over the carbon allotropes is of interest. Transmission electron microscopy and related techniques are gaining more and more importance in the study of nanoscale hybrid materials. Owing to new advances such as aberration correction, atomic column imaging and spectroscopy at low voltages and electron tomography, a comprehensive understanding of the interfacial phenomena is possible. Moreover, 3D tomography combined with other techniques responds to important questions such as coverage yield along with information on chemical, structural, electrical and magnetic properties of carbon based hybrid materials.

Keywords: hybrid materials; graphene; CNT; STEM; electron holography; electron tomography; Cs correction; Cc correction; low voltage S/TEM; EELS; EFTEM; EDX, ETEM

1. Hybrid materials at the nanoscale

Hybrid materials present one of the most fascinating properties with applications in sensors, solar cells, Li-ion batteries among others [1-3]. Moreover, the ability to combine two different classes of materials at the nanoscale has always remained enticing for many different researchers. In a hybrid material, two different materials where one is organic and the other is inorganic are usually coupled. The organic constituents range from carbon allotropes to polymers, while the inorganic component usually comprise of metals or metal oxides. The type of bonding (ionic, covalent...) in these materials is rather variable depending on the liaison at the interface. As these materials, like any other nanomaterial, contain most of the atoms on their surfaces, the interaction between their surfaces when combined, plays a dominant role in their physical properties. Surface related phenomena are not only linked to surface atoms but also to adatoms or functional groups present on their surfaces. The physical properties obtained by combining such materials results in a hybrid material possessing the characteristics of the individual materials and the new properties as a result of hybridizing [4; 5]. Carbon based hybrid materials are usually combined with metal or metal oxide nanostructures synthesized in nanoparticles or thin films. Carbon allotropes come in various dimensionalities 3D (diamond), 2D (graphene), 1D (carbon nanotubes or CNT) or even 0D (fullerenes C60, C70, C82...)[6]. Studying carbon chemistry which consists of analysing various hybridizations in the carbon matrix viz., sp², sp³ or sp⁴ forming π or σ bonds is routinely carried out in Energy Electron Loss spectroscopy (EELS) in a Scanning/ Transmission Electron Microscope (S/TEM) [7]. In fact, EELS is capable of discerning the type of hybridizations occurring in the carbon matrix; for example, diamond is an exclusively sp³ hybridized carbon allotrope. On the other hand graphene, is exclusively sp² hybridized, while as other allotropes such as CNT or diamond like carbon, possess both, sp²-sp³ hybridization. The EELS edge positions and the aspects of the peaks of the Electron Loss Near Edge Structure (ELNES) signal of the C-K edge are invaluable in obtaining the electronic structure of the material.

Furthermore, when these carbon allotropes are combined with nanoparticles (NP) the interface of the CNT-NP shows changes in the hybridization which are generally indicative of a change in the physical properties of the material. Even the defects in such an allotrope, be it at the interface, on the nanoparticle or in the carbon matrix, are decisive in determining the physical properties of the material as a whole. These defects are rather easily studied by modern TEM imaging and analysis employing Cs+Cc correctors, monochromators, EELS, energy dispersive x-ray spectroscopy (EDX), electron holography and electron tomography. In fact, electron tomography which allows 3D imaging of a nano-object has become a routine and versatile technique. Indeed, the selective decoration of these nanoparticles is of interest as now-a-days, researchers are looking for optimal coverage yields. Therefore, probing the atomic, chemical and electronic structure at the interface provides useful information on the propensity of the nanoparticles to adhere to certain anchorage points in order to optimize the coverage. In this regard, obtaining this information in 3D is the need of the hour. Furthermore, electron tomography that is now capable of assimilating EELS, EDX and electron holography among others, consequently provides simultaneous chemical, structural, electronic and even magnetic information in 3D.
This book chapter aims at bringing forth different analysis techniques that are currently being used in a S/TEM for the characterization of hybrid materials incorporating the most popular carbon allotropes viz., graphene and CNT. Moreover, the chapter also provides the advantages and drawbacks of various techniques related to the nanoscale observations of CNT and graphene based hybrid materials. State of the art, new generation microscopes and their capabilities in observing hybrid materials are also brought into the limelight.

2. Challenges and progress in observing hybrid nanomaterials via S/TEM

With regards to their observation and analysis with the help of transmission electron microscopy, the recent progress in imaging techniques by addition of Cs correctors and probe correctors, has made sub-Ångström atomic column resolution possible. Since the past few years, acceleration voltages of 200KV-300kV were common. The disadvantage of using high acceleration voltages on a carbon based sample is twofold: beam damage not only breaks carbon bonds and degrades the sample but also the building up of carbon contamination makes imaging difficult. This contamination has a tendency to corrupt elemental identification and quantification. Several preventive measures exist for alleviating the carbon contamination, which include storing the sample in the sample holder under a pumping station for a long period to evacuate contamination. Plasma cleaning as an option, even though commonly used, has various disadvantages. In fact, plasma cleaning on thin films or bulk samples has proven to be effective in reducing hydrocarbon species and has provided better imaging conditions in aberration corrected microscopes. This is because, during plasma cleaning, the carbon contamination reduces exponentially with the increase in plasma cleaning time [8]. However, in the case of carbon based materials deposited on a carbon coated TEM grid, the plasma etching is too harsh for not only the carbon coating of the grid but also for the hybrid material itself. Disadvantageous consequences include the destruction of the holey carbon layer or perforations in the uniform carbon layer of the support grid. Moreover, perforations in the carbon film cause detachment of the carbon film from the Cu grid which then folds on itself, creating a very thick phase specimen and making high resolution observations unlikely. Moreover, detached carbon films are unable to evacuate charges and cause instability in the sample. To obtain more efficient and softer plasma cleaning, pulsed plasma cleaning is used [9]. This consists of a few seconds of plasma pulses that help reduce the plasma intensity for delicate samples. With such a type of plasma cleaner it is also possible to monitor the plasma pulse intensity during operation and is more adapted to carbon based materials.

Another method of reducing carbon contamination for TEM/STEM observation would include lowering the acceleration voltage of the microscope to 60KV or 80kV and overcoming the knock on voltage for carbon. In the past, lower acceleration voltages tended to lower the spatial resolution in a conventional TEM. The reason being that in TEM, the resolution depends directly upon the De Broglie wavelength of the electron which in turn, is inversely proportional to the accelerating voltage. However, in STEM the resolution is equal to the size of the probe. Nevertheless, for low-voltage observations, when the acceleration voltage is decreased the spherical aberration (Cs) is increased and resolution is decreased; Cs correction for the probe forming lenses then becomes necessary in STEM. Now-a-days, it is possible to combine a monochromator with a probe corrector in STEM to reduce the energy spread of the probe or suppress the ‘rainbow effect’. Moreover, acceleration voltages as low as 30kV have been used to achieve atomic resolutions of graphene in STEM by increasing the convergence angle and overcoming the diffraction limit of the electrons [10]. On the other hand, in low voltage TEM, the information limit as obtained from the phase contrast is also dependent on the chromatic aberration (Cc). This implies that, even though the Cs is reduced to micrometres and is capable of providing sub-Ångström resolution; further improvement in the resolution becomes difficult as the Cc becomes the resolution limiting factor. The SALVE project combines the benefits of Cc and Cs correction at voltages as low as 20-80 kV providing sub-Ångström resolutions with very little probability of damaging the hybrid materials during observations[11].

3. Hybrid materials as supports for TEM observations

Other than exploring their very particular physical properties, hybrid materials have also been used for TEM sample supports facilitating observations of the inorganic counterpart [12]. The organic constituents are either graphene or CNT while the inorganic parts are usually nanoparticles. Using conventional TEM grids such as holey carbon or carbon films can also give information about the morphology, size and agglomeration. However, in case of the nanoparticles encapsulated in an amorphous or very thin crystalline shell, the contrast from the thicker carbon grid does not help in discerning the thin shell. In one research work, the authors have synthesized aerosol particles such as SnO2 and Ag which were then combined with CNT on bare copper grids[13]. The study proved efficient in illustrating that the nanoparticles had an amorphous shell which would have not been possible with a conventional carbon coated grid. The observation was conducted on particles protruding from the side walls of the CNT. A large area of the particle was suspended in vacuum and was therefore available for observation, as explained below. In fig. 1(a) super-aligned CNT on which Au NP are deposited is presented. The CNT bridges the holes in a copper mesh grid and strategically places the nanoparticles within these holes. In figure 1(b) A HRTEM image of the Au NP is provided and clearly manifests the
shell around the Au NP. Graphene oxide as a support for nanoparticles has also been tested [14]. The studies suggest a reduced electron scattering compared to the conventional TEM carbon grids which engenders an improvement in the image contrast. Moreover, graphene oxide is highly stable and encourages the decoration of hydrophilic water soluble molecules or nanoparticles with functional groups.

Figure 1: TEM image of synthesized super aligned Carbon Nanotubes used in a TEM grid, harboring gold nanoparticles. Adapted with permission from [15] Copyright (2016) ACS.

4. Imaging of hybrid materials on a Scanning/Transmission Electron Microscope

4.1 TEM imaging

TEM imaging is the most widely used TEM technique in studying hybrid materials. This is due to the fact that it provides instant information on the hybrid material with regards to its morphology as in fig. 2a, where a ZnO NP adheres to a CNT [16]. Other important aspects such as, qualitative coverage of nanoparticles on the carbon based materials can be obtained at a quick glance. Furthermore, topological defects such as bends in CNT and creasing in graphene are readily observable which further facilitates the understanding of selective decoration of the NP. Moreover, filled nanotubes as well as decorated nanotubes are becoming popular as there is a constant need to increase surface coverage of these structures. High resolution transmission electron microscopy (HRTEM) provides us with information about atomic configuration of the carbon matrix (armchair, chiral or zigzag for CNT), of the defects and the quality of the hybrid interface. The latter is more adapted with electron tomography explained later [17]. In figure 2(b), HfO₂ NP adhere to the outer-wall of the CNT [18]. Even though atomic column imaging of the CNT is not possible as the point to point resolution is 2.2Å of the microscope in TEM mode operating at 200kV, information on the quality of the walls, crystallinity of the NP are readily available. Nevertheless, aberration correction has proven to be advantageous for HRTEM imaging when considering the reduced inelastic scattering and sharper atomic column imaging of the π bonded C atoms. Moreover, background contributions from the amorphous carbon grid are diminished as the real working defocus remains ± 10nm much lower compared to the Scherzer defocus in non-Cs corrected HRTEM [19].

Figure 2 (a) conventional low magnification TEM image of ZnO-CNT structures. Adapted from Ref. [16] under creative commons attribution licence, (b) HRTEM image of HfO₂ nanoparticles on one of the side walls of the CNT. Adapted from Ref. [18] under creative commons attribution licence, (c) Cs corrected HRTEM image of Pt nanoparticle filled in a CNT. Adapted from Ref. [20] copyright 2016 RSC , (d) HRTEM image acquired with the SALVE III TEM at 30kV. Adapted from web page Ref. [11].

In figure 2(b), Cs corrected TEM clearly highlights the atomic arrangement of the CNT possessing a zigzag arrangement of the C atoms as well as the Pt nanoparticle along the (001) direction [20]. Moreover the CNT walls contain amorphous carbon and the carbon from the support grid shows minimum contrast. Furthermore, at such small defoci the lattice delocalization is reduced thereby facilitating artefact-free imaging conditions. This implies that Cs corrected microscopes can be operated with a homogenous transfer up to the information limit unlike non-Cs corrected TEM [21; 22]. Low voltage TEM has also been conducted on various carbon materials. Especially interesting is the Cs and Cc, double corrected TEM where voltages as low as 30kV can provide atomic resolution in carbon based materials. In fig. 2(d) clear atomic arrangements of C60 fullerene within a SWCNT are visible at 30kV acceleration voltage [11].
4.2 STEM imaging

As discussed in section 2, considering the large amount of carbon contamination produced during STEM operation at 200kV or 300kV, STEM imaging becomes a challenge. It is well known that the contamination is a result of hydrocarbon bond breaking which is present everywhere in the carbon based sample as well as in the vacuum system. Solutions to surmount this problem include, cleaning the column via a baking out or a cryo-cycle which reduce the contamination. However, there is always a residual contamination or contamination that builds up during observation even after adapted plasma cleaning of the sample. Consequently, a growing contamination reduces image contrast. Moreover, the number of carbon atoms deposited remains constant over time. The carbon contamination while working with high resolution STEM therefore appears to be enhanced as the observed area is reduced to a few atomic columns. Once again plasma cleaning of carbon based samples is complex and contamination can only be reduced when making observations at low magnification or working with low voltages of 60kV or 30kV. Nevertheless, 80kV acceleration voltage proves to be a little better than working with higher voltages, however, it is still preferable to work under 60kV as materials such as nanocarbon allotropes can be damaged at a threshold voltage of 60kV due to knock on damage [23]. Low voltage STEM has been used to study CNT filled carbide nanostructures. The images presented were high contrast, obtained in a SEM operating at 5kV fitted with a STEM detector with a point to point resolution of 5nm [24]. Nevertheless, observing single atoms in carbon allotropes without causing irradiation damage and successfully obtaining a point to point resolution under 1Å, is possible as has been shown in the case of graphene at 60 kV [25].

Figure 3: (a) HAADF-STEM images of Fe-N doped CNT sample. Adapted from Ref. [26] copyright license 3990101001408, (b) HAADF-HRSTEM images of HfO$_2$ decorating carbon nanotubes. (c) topological defect on a CNT on which nanoparticles are anchored. (b) and (c) adapted from Ref. [18] under creative commons licence attribution, (d) HAADF-HRSTEM image of graphene showing the hexagonal arrangement of carbon atoms. Adapted from Ref. [10] copyright license 3990101300811.

In figure 3(a) a low magnification HAADF-STEM image was captured at 200kV acceleration voltage showing minimal carbon contamination [26]. The sample consisted of N doped CNT decorated with Fe nanoparticles. Information on the coverage of the NP along with the presence of amorphous carbon is easily obtained. In figure 3(b) HfO$_2$ nanoparticles decorating CNT are presented [18]. Even though, the accelerating voltage was reduced to 80kV the carbon contamination could not be eliminated considering the very high magnification; therefore, imaging the tube walls was no longer possible. Nevertheless, atomic column imaging of the HfO$_2$ nanoparticles was possible but due to the carbon contamination, obtaining a point to point resolution of 0.8Å proved to be a challenge. Similarly in fig. 3(c) for shorter observation times, defects such as wall bending were visible along with atomic column imaging of the HfO$_2$ nanoparticles. Graphene was also observed with Low Angle Annular Dark Field (LAADF)-STEM at 30kV acceleration voltage where clear hexagonal arrangement of the π bonded C atoms is visible. Such low energy conditions are ideal for STEM imaging [10].

5. S/TEM related spectroscopic techniques

5.1 EDX

The necessity of chemically analysing a nanomaterial at the nanoscale or at the atomic scale is quite clear when considering the dimensionality of the nanomaterial. For ex., one HfO$_2$ nanoparticle of 2nm in size with a lattice parameter of 0.5Å would contain 212 atoms and being able to chemically identify each atom, even though not routinely carried out, is possible today. EDX is one such technique that identifies chemical species in the sample. The principle of EDX is based on the interaction of the electron beam with the sample producing X-Rays. Identifying the X-Ray energy which is quantified provides the signatures of the elements present in the material. Sometimes, a quick qualitative analysis is enough to check the presence of elements in the material. At other times, in the case of doping, finding the quantity of the dopant is also required. In a TEM, EDX point analysis is easily performed and spectrum provides precise information of the concentration of elements. Spectrum processing by background signal removal is necessary to give accurate values of concentrations. In principle, the accuracy increases with recording time but in carbon based hybrid
material recording time needs to be reduced to decrease carbon contamination. In STEM, other than point analysis other kinds of analysis such as line scans to identify elements and their quantities on points over which the probe moves linearly can also be performed. The path taken by the probe is defined by the user and could be along the interface of a hybrid material. In EDX mapping of a zone, the probe rasters over a predefined area and the detector records individual photon signals. It provides a spatial distribution of various elements in a sample in a user defined zone.

![Figure 4](image-url)

**Figure 4** (a) Pt- N doped graphene STEM image used for EDX analysis. Inset shows the EDX spectra from the zone of interest. (b) Mapping of the Pt peak indicating the distribution of Pt nanoparticles in graphene. (a) and (b) Adapted from Ref. [27] Copyright license: 39901100680734 (c) STEM image of N doped CNT with Co nanoparticles. Inset relates to the elements present in the zone of interest, (d) C (e) Co and (f) N maps in the sample. (c), (d), (e), (f) adapted from Ref. [28] copyright license: 3990111044834, (g) Pt impurity atom in STEM image. Atomic column EDX indicating the atomic impurity to be Pt. Reproduced from Ref. [29] copyright license: 3990120047657.

Silicon Drift Detectors today show very high sensitivity and one is able to create maps in minutes. Maximizing the number of counts is now made available by placing 4 Solid State Detectors as in in a FEI Titan G2 80-200 fitted with a ChemiSTEM™ [30] placed symmetrically around the sample which efficiently collects x-rays, especially in the case of a low number of counts. This implies that quantitative assessment of carbon based materials doped with light elements such as B, F or N is also possible. In figure 4(a), a STEM image of N doped graphene loaded with Pt nanoparticles is present. The EDX spectrum of the zone provides elements such as C, N, Pt and Cu originating from the TEM support grid. An elemental mapping of the zone was carried out with X-Ray M line for Pt and clearly indicates a uniform distribution of the Pt nanoparticles. Similarly for Co decorated N doped CNT in figure 4(c), a similar elemental mapping can be performed [28]. Individual elemental maps of each i.e. C in figure 4(d), Co in figure 4(e) and N in figure 4(f) further elucidate the respective elemental distributions. The HAADF-STEM image is useful when studying the C map as one is able to distinguish between the C of the CNT and that of the carbon grid. In a STEM providing sub-Å resolution atomic column, EDX is also possible. For example Pt atomic inclusion in graphene was reported with a probe size and current of 1.4nm and 190pA respectively [29]. In figure 4(g) the single Pt atomic impurity was isolated by low voltage STEM and the element was confirmed by placing the probe on the impurity and obtaining an EDX spectra in figure 4(h) where the Pt signal is clearly visible.

5.2 EELS

For carbon based hybrid materials, core loss EELS or ELNES of the C-K edge locally probes the electronic structure of the carbon based material after interpreting the peak position and features visible in the edge [18]. Two distinct peaks are usually visible in the C-K edge of carbon based materials (graphene or CNT) which correspond to the \( \pi^* \) and \( \sigma^* \) peaks. The \( \pi^* \) peak at 285eV corresponds to the \( \pi^* \) transition or the transitions taking place from the 1s to unoccupied antibonding \( \pi^* \) state; whereas, the exciton peak \( \sigma^* \) at 292eV arises due to transitions to the antibonding \( \sigma^* \) states in the
CNT. These transitions are clear indications of the types of hybridization that carbon nanomaterials undergo. Moreover, the profiles and ratios of the $\pi^*$ and $\sigma^*$ peaks give us further indications on the type of carbon bonding, crystallization, damage to the walls of the carbon nanotubes and the presence of functional groups. It also indicates the proportion of carbon atoms undergoing sp$^2$ or sp$^3$ hybridization. The smearing of the $\pi^*$ and $\sigma^*$ peaks are attributed to disordered carbon atoms or amorphous carbon. Other peaks at 288.2eV are related to carbonyl (C=O) and at 289.7eV is related to carboxylic (–COOH). ELNES performed with a monochromator disposing an energy resolution of 0.2eV was used to study the functional groups on the side walls of the CNT after they were acid treated; the peak at 287.7eV was attributed to carboxylate functional groups and further corroborated with DFT calculations [31].

Figure 5: (a) HAAD-STEM image produced by the same beam settings used to acquire EELS spectra in, (b) the number indicates areas at which the EELS spectra were acquired. (a), (b) reproduced from Ref. [18] under creative commons attributions licence (c) EELS spectra for various Au alloys on graphene. Reprinted with permission from [34]. Copyright (2016) ACS.

Furthermore, monochromated EELS where energy resolutions of 20meV along with 1Å probe, has advanced the understanding of the electronic structure of materials [32]. For example, in a Si-CNT based hybrid material for Li ion batteries, studying the Si-L edge and the C-K edge has shown the formation of Si-C bonds at the interface [33]. The formation of the Si-C bond makes the material robust even after lithiation and delithiation processes. Moreover, it has been shown that decrease in the $\pi^*$ peak intensity indicates an increase in sp$^3$ carbon fractions when Fe$_2$O$_3$ nanoparticles are attached to the CNT [35]. Similar changes were observed for graphene decorated with metal nanoparticles. In figure 5(b) a HAADF-STEM image captured at 80kV acceleration voltage of the CNT decorated with HfO$_2$ is presented [18]. The image appears hazy as the STEM image was acquired with a probe aligned and optimized for EELS. The EELS spectra in figure 5(b) correspond to certain points on the CNT. Probing the electronic structure locally is necessary to understand how the C atoms facilitate the anchorage of HfO$_2$ nanoparticles. Furthermore, at the interface of the HfO$_2$-CNT hybrid, the carbon atoms are disordered along with wall damage as seen from the featureless hump which also indicates the presence of amorphous carbon. Carbon dangling bonds are usually present in amorphous carbon; they bond with the organic constituents surrounding the HfO$_2$ nanoparticle. This is a plausible explanation for the decoration of the HfO$_2$ on CNT. In the case of, Au and Au-alloys such as AuIn and AuGa decorated on graphene [34], in figure 5(c) various ELNES spectra are provided to study the C-K edge of graphene. AuIn and AuGa decorated graphene both have their $\pi^*$ peaks shifted to higher energies also interpreted as a local increase in net charge of the C atom, indicative of an electrostatic bond. Here, there appears to be a charge transfer from the Au and Au-alloy nanoparticles to graphene. The alloys also generate an increase in the sp$^3$ hybridization as evidenced from the features in the $\sigma^*$ peak.

5.3 Energy Filtered Transmission Electron Microscopy (EFTEM)

EFTEM combines the imaging capabilities of a TEM and the spectroscopic capabilities of EELS [9; 36]. Images thus obtained are filtered either in energy and provide compositional maps with high lateral resolution. EFTEM is different from spectral imaging (SI) as the former is carried out in a TEM i.e. a parallel imaging mode while as the latter is carried out in a STEM where EEL spectra are recorded from each point on the specimen in a sequential manner [37]. The limiting resolution in EFTEM images is due to the spatial delocalization of inelastic scattered electrons and aberration of the lenses. Energy filtering is performed with the zero loss peak, plasmon peak or the core loss edges. For example, filtering out the zero loss peak in EELS helps reduce inelastic scattered electron or the energy spread due to sample thickness effects. Plasmon peak filtering is useful when nanocomposites with different compositions need to be singled out. Core loss EELS edges turn out to be useful in mapping EFTEM images when the plasmon peaks of certain compounds tend to overlap. Furthermore, ELNES is capable of mapping variable chemical bonding states for a given element. Moreover, distribution of doped species in the CNT such as N, B are more easily detected and studied with EFTEM as light element analysis is one of the major advantages of EELS. Even though, light elements have been
but also indicates that graphene covering the CNT harbours more defect sites. K-edge map illustrates high N concentration on walls possibly originating from the 2D projection of the CNT in a TEM that other techniques as explained in section 6, are more adapted to studying filled CNT. Finally, in figure 6(e), the N edges and indicate that the majority of the nanoparticles are on the outside of the nanotubes. It is important to mention a result of nanoparticle decoration. In figure 6(c) and (d) the Co and O distribution are obtained with Co-L and O-K sample. The difference in contrast is the CNT core which is brighter and the graphene shell which appears to be flaky as decorate Co3O4 nanoparticles [40]. TEM imaging was carried out prior to EFTEM. In figure 6, the EFTEM maps of various elements are presented. Figure 6(a), the TEM image of the zone of interest is presented where nanoparticles decorate the N doped carbon based material. In figure 6(b) the C-K edge was mapped out to localize carbon in the sample. The difference in contrast is the CNT core which is brighter and the graphene shell which appears to be flaky as a result of nanoparticle decoration. In figure 6(c) and (d) the Co and O distribution are obtained with Co-L and O-K edges and indicate that the majority of the nanoparticles are on the outside of the nanotubes. It is important to mention that other techniques as explained in section 6, are more adapted to studying filled CNT. Finally, in figure 6(e), the N K-edge map illustrates high N concentration on walls possibly originating from the 2D projection of the CNT in a TEM but also indicates that graphene covering the CNT harbours more defect sites.

6. Tomography

Electron tomography is one of the fastest growing techniques in materials science even though it has conventionally been used in 3D analysis of biological samples [41]. The 3D disposition of hybrid materials especially in the case of catalysts, provides explanations on their selectivity in catalytic reactions [42]. Moreover, electron tomography can be used in both TEM and STEM modes [43]. TEM mode tomography presents a few limitations such as diffraction and phase contrast which can be overcome in STEM-ADF tomography. However, other factors come into play with STEM such as damage to specimen and limitations to tilt due to geometry of the sample. However, in the case of CNT which is a needle shaped structure, the geometry of the sample is no longer a drawback [44]. Today, it is possible to obtain atomic column imaging in tomographic images by using the centre of mass alignment procedures [45]. In electron tomography, tilt series are performed and images are captured at every 2° or 1° tilt from ±75°. The tilt series are then reconstructed after obtaining accurate spatial alignment, determining tilt axis and assuring that the tilt series were performed at accurately determined tilt angles. In the case of porous carbon materials or carbon nanotubes, tomography provides irrefutable proof of the position of the nanoparticles i.e. whether they lie inside or outside the pores or walls. Recently, a tomographic study on a hybrid structure of CNT with Fe3O4 nanoparticles was carried out and views along the ZY planes are illustrated in figure 7(a, b) [46]. With the help of tomography, the authors have concluded that the inner tube of the CNT was indeed filled with Fe3O4 nanoparticles as shown in the slices of the top view figure 7(c) and (d). They further observed that the Fe3O4 nanoparticles were not tightly packed and therefore did not clog the tube, implying that there is still room for gaseous reactants to circulate within, during gas sensing activities. This furthermore implies that defect sites are present within the CNT and are available for anchorage of Fe3O4 nanoparticles suggesting a larger active surface area is available for catalytic activities. After tomographic reconstruction, they were able to illustrate the filling and decoration of the CNT as shown in figure 7(e). In another study with the same kind of nanocomposite, tomography aided in understanding the impact of sonication in the filling of nanotubes [35]. Authors have observed holes in the CNT walls which in fact serve as pathways for the precursor to form nanoparticles within the CNT. On a similar note, a hybrid structure made of graphene-Au nanoparticles employed as trackers, are used by
biologists to align tilt series for electron tomography [47] with variable concentrations of Au depending on the magnification used to perform the tilt series.

Figure 7: (a), (b) TEM tomographs of Fe₃O₄- CNT showing selective filling of CNT viewed along XY axis, (c, d) along XZ or top view of CNT, (e) reconstructed volume showing the disposition of the nanoparticles (red) in the CNT. (a-e) reproduced from Ref. [46] copyright license: 399013064496, (f) field of view of 0° tilt acquired from tilt series of gold nanoparticles on graphene used for aligning the tilt series [47] creative commons license attribution.

7. Electron holography

Electron holography performed in a TEM is a technique that can record the hologram which includes amplitude and phase profiles, of the electron wave passing through an object. The phase profile of the hologram has been used to study the electrostatic potentials and magnetic fields in a material. It has also been used for calculating the morphology and diameter of CNT [48]. In off axis electron holography, the specimen is examined with a highly coherent beam. A voltage is applied to an electron bi-prism which deflects the electron beam that has passed through vacuum. The latter then interferes with the wave having passed through the specimen and the interference pattern then creates a hologram. The objective lens is turned off when working with magnetic materials as it creates a parasitic magnetic field in the electron beam direction [49]. Electron holography has proven to be useful in understanding the magnetic properties of CNT filled with iron nanoparticles. The study has shown that the iron nanoparticles that are ellipsoidal in shape contain single domains of magnetic field. Also, magnetic field interactions of the nanoparticles closely spaced to each other were studied. Electron holography therefore has the advantage of being able to study local magnetic or electrostatic fields and magnetic domains at the nanoscale.

8. In-Situ S/TEM

8.1 Catalytic observations

In-situ TEM or environmental TEM (ETEM) studies the nanostructure and morphology of a material, under the influence of gases and temperatures. The technique also provides information on for example, the catalytic activity of the material in real space and time and provides direct insight on the transformation of the material, if any [50]. For example, ETEM studies on various catalyst nanoparticles have illustrated in real time, the formation of carbon nanofibers or graphene sheets when exposed to certain gases [51]. For example Ni [52], MgO supported Pt [53] and Fe [54] nanoparticles have proven to have active sites for the growth of carbon based materials when exposed to methane. Moreover, other studies on CNT have demonstrated the resistance of the CNT to oxidation under O₂ flow, depending upon the number of walls on the CNT [55]. Moreover, studies under H₂ gas conditions for catalytic activities in water splitting experiments, have also been carried out [56]. However, these methods allow a fundamental understanding of the material and cannot be used as a regular method for producing hybrid material structures. Furthermore, beam damage is also an important problem when analysing beam sensitive materials with such a technique. In fact, damage can create active sites in the nanoparticles which were not generated during the growth itself and can promote the growth of carbon based materials [57].

Nanoparticle channeling in graphene has been a keen research subject whereby, the metal nanoparticle follows certain pathways defined by crystal lattice direction [58]. This was observed in ETEM experiments where a graphene-silver nanoparticle hybrid was heated to temperatures from 600- 800 °C and exposed to different O₂ flow rates. The experiment provides the channeling direction to be (100) and presents the behaviour of the metal nanoparticles under catalytic experimental conditions along with the possibility of nanoscale patterning. Another study recently conducted, showed that the interface between CNT and Ag was oxidized when exposed to O₂ arriving at the interface via the Ag₂O₃ oxidation [59]. Filling of Sn in carbon nanofibers has also been probed by ETEM and a mechanism of Sn filling in the
carbon nanofibers, was proposed. Here, however the diffusion dynamics of Sn was probed by only heating the sample up to 400°C without the use of gases [60]. In all the above cases, structural and spectroscopic analyses were carried out in the TEM for comparison of the materials before and after ETEM experiments.

8.2 Electrical measurements

Electrical properties of carbon nanotubes can also be studied by in-situ techniques in a TEM. The behaviour of the CNT under electrical currents is interesting for application in nanoelectronics and optoelectronics, among others. Joule heating was studied in-situ for Zn0.92Ga0.08S@CNT where the CNT encapsulated the ZnGaS gas with the help of a two terminal electrical contact within a TEM [61]. These hot spots and local heating have been further monitored in a TEM by determining the temperature with the help of a probe placed at a given point [62]. In such experiments, contribution of heating due to the electron beam needs to be evaluated. A nano-thermocouple of Cu and Ni-Cu tips, movable with nanoprecision was used for the same. The nanothermocouple used in the experiments was directly attached to a CNT. Moreover, electrochemical studies such as lithiation and delithiation in Li –ion batteries, have also been conducted from a fundamental point of view. In-situ lithiation and delithiation in TEM, of Si-graphene hybrid has helped in understanding the large volume change of Si bonded to graphene when alloyed with Li at the atomic scale [63]. Here lithiation-delithiation was realized via a ±3V bias current applied to the Si-graphene sample where the LiO2 was used as a lithium source. The spiking in current during observation, was also explained on the basis of agglomeration of Si nanoparticles forming larger nanoparticles. Nevertheless, graphene was considered to efficiently reduce the electrochemical sintering of Si. With further regards to graphene, the effect of wrinkles on its electrical properties has also been studied. Wrinkled graphene shows lower resistance, possible due to a large area contact with the probe and is a proven electrically robust material [64].

8.3 Mechanical measurements

Challenges in mechanical measurements arise mainly due to the nanosize of the carbon based materials and the difficulty in getting a hold of them in order to determine for example, their mechanical strength [65]. Elasticity of the CNT is carried out by charging CNT and applying a current at its tip which in turn, bends the CNT due to electrostatic forces. By alternating the charge at the tip, one is capable of obtaining the elastic limit by creating a cyclic charge loading of the CNT. Moreover, a nanobalance can be created by attaching a nanoparticle to the tip of the CNT and vibrational frequency is determined in order to calculate the spring constant. Tensile strength of a graphene sheet was also tested. A fractured graphene sheet was used for the procedure where the fracture was treated with amorphous carbon. On increasing voltage, the amorphous carbon showed poor adhesion and broke away indicating that graphene had a higher tensile strength than amorphous carbon [66]. Mechanical collapse can therefore be evaluated before conducting the electrical measurement on such structures [67]. Moreover, for lithium ion batteries, even during lithiation, graphene proved to be more resistant and robust towards fracture than CNT [68].

9. Conclusion and perspectives

In the last 20 years the development of carbon based hybrid materials has taken a giant leap forward, along with the progress in transmission electron microscopy and related techniques. Characterizing them at the nanoscale has been the major breakthrough in studying their morphology, chemical composition, electronic structure and their 3D disposition. Aberration corrected (S)TEM has brought along new perspectives to their observation in terms of spatial resolution. For example, in a conventional TEM the spatial resolution is around 100Å with λ being the Debroglies wavelength. Introduction of a Cs corrector has increased spatial resolution by around 60% and double correction (Cs and Ce) has further increased the resolution by another 20%. This clearly suggests a very high resolution or sub-Å resolution at 40–80kV acceleration voltage and precise atomic column positioning with 1 pm accuracy. Furthermore, other advantages such as low radiation damage especially concerning carbon based hybrid materials; HRTEM and tomographic analysis of thicker samples and atomic column resolution using EFTEM, also exist. Moreover, in-situ experiments also benefit from these advances and better resolution in ETEM experiments are observed. This has further opened new avenues to techniques such as holography where magnetic and electrostatic fields can be mapped out with very high spatial resolution.

Combination of various techniques in TEM to study a hybrid material is rather common and is necessary. Such techniques include (S)TEM-EELS, (S)TEM-EDX, (S)TEM-holography, (S)TEM-Tomography. Combining such techniques has provided us with simultaneous structure and chemical information; morphology and crystal structure information; morphology and 3D information and morphology with magnetic or electric potential information.

Moreover, electron tomography has proven to be the only technique able to distinguish between a filled or decorated CNT and whether or not the nanoparticle lies below, above or in between graphene sheets. Electron tomography can also be combined with for example a spectroscopic analysis such as EELS [69]. Here for example preferential decoration of nanoparticles due to superficial selectivity to such carbon based structures can be assessed along with
their doping. Such 3D information could further help in understanding various physical properties of the material such as, catalytic, electrical, optical or magnetic properties.

A thorough comprehension of the structure of the materials along with its magnetic properties is currently focused upon as magnetic ordering at the nanometer scale can now be directly obtained. This has advanced understandings of magnetism and spintronics [70]. Electron holography tomography is one such ‘hybrid’ technique that allows such analyses. In fact, electron holography provides a 2D representation of a magnetic field in one particular direction of the electron beam. The 3D representation of the magnetic field is then extrapolated from simulations. When combining the electron tomography with holography, holograms can be obtained for various tilts. One is therefore capable of obtaining tilt series of projected electric and magnetic potentials which are then used as input data for tomographic reconstruction [71]. Electrostatic potentials could also provide information on the decoration of nanoparticles by mapping out electrostatic fields at such anchorage points as interfacial phenomena play an important role in such materials, when considering their physical properties.

The research on carbon based materials hybridized with nanoparticles has taken a leap forward. The importance is in understanding the interface and the defect related phenomena created by interfacial properties and tailor materials for innovative applications. In fact, this interfacial phenomenon tends to affect the electronic, structural, optoelectronic, electrical, chemical thermal and mechanical properties of such structures. This new era of transmission electron microscopy combines Cs-Cc corrections and sub-Å resolution with minimum beam damage owing to low voltage operations. In the past, 2D structural, morphological, electronic structure and chemical analysis were routinely done on these carbon based structures but now 3D analysis is more and more widespread, pushing fundamental understanding of carbon based hybrid materials to the atomic scale.

**Acknowledgements:** The authors would like to thank the the Estonian Research Council (grant PUT431), the European Regional Development Fund project TK134 (TARI6019) for financial support.

**References**


