Characterization of nanomaterials with transmission electron microscopy

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Abstract. The field of nanotechnology is about research and development on materials whose at least one dimension is in the range of 1 to 100 nanometers. In recent years, the research activity for developing nano-materials has grown exponentially owing to the fact that they offer better solutions to the challenges faced by various fields such as energy, food, and environment. In this paper, the importance of transmission electron microscopy (TEM) based techniques is demonstrated for investigating the properties of nano-materials. Specifically the nano-materials that are investigated in this report include gold nano-particles (Au-NPs), silver atom-clusters (Ag-ACs), tantalum single-atoms (Ta-SAs), carbon materials functionalized with iron cobalt (Fe-Co) NPs and titania (TiO₂) NPs, and platinum loaded Ceria (Pt-CeO₂) Nano composite. TEM techniques that are employed to investigate nano-materials include aberration corrected bright-field TEM (BF-TEM), high-angle dark-field scanning TEM (HAADF-STEM), electron energy-loss spectroscopy (EELS), and BF-TEM electron tomography (ET). With the help presented of results in this report, it is proved herein that as many TEM techniques as available in a given instrument are essential for a comprehensive nano-scale analysis of nano-materials.

1. Introduction
The field of nanotechnology deals with the science, engineering, and technology of materials whose at least one of three dimensions is in the range of less than one hundred nanometers [1]. The modern concept of nanotechnology was introduced by 20th century celebrated Physicist Richard P. Feynman in which he proposed the use of 1 nm³ size clusters as “computer bits” [2]. It is to be noted that TEM was most elaborate and powerful technique that was available for the imaging of materials. However due to inadequate spatial resolution, the TEM instruments was unable to meet the challenges of imaging such underlined one nm size atom-clusters. This is why Feynman stressed upon improving the spatial resolution of TEM instruments [2]. Albeit not related but there had been consistent efforts in improving the resolution and capability of TEM instruments [3-4]. One of most important developments in this regard is arguably spherical aberration correctors for both conventional TEM and scanning TEM (STEM) modes of TEM instruments [5-6]. With the help of such correctors, the contemporary TEMs are capable of providing atomic scale imaging, elemental and chemical analyses of samples [7-9].

A complete introduction about a TEM instrument is beyond the scope of this report. As there are number of textbooks are currently available on this technique [10-13]. Nevertheless for the sake of completeness a brief introduction is given in this report to highlight the most important parts of TEM instruments. As an aside, it is imperative to note that the thickness of materials in the direction of
penetrating electron beam is crucial for their TEM analysis. In fact this thickness has to be below the value of about 500 nm in order to have the enough fraction of electron beam transmitted through sample elastically which is a prerequisite to the formation of TEM-images. It is also essential that the electrons, provided by a thermionic or a field-emission gun, are collimated nicely with the help of electromagnet condenser lenses prior to their passing through the samples. A number of interactions take place between the sample atoms and penetrating electron beam when it passes through the samples. The transmitted electrons are then focused by using another electromagnetic lens called the “objective” lens which forms the first image of samples. The resolution of images formed in TEMs depends upon the wavelength of electrons used as well as the value of spherical aberration co-efficient (Cs) of the objective lens. As a practical fact, a typical resolution of an image in contemporary TEM instruments is in the range of 0.2 nm without using a spherical aberration corrector (Cs-corrector). Whereas the spatial resolution of 0.05 nm can be reached for both TEM and STEM modes by employing Cs-correctors after and before the samples, respectively [10,12]. Likewise the image-plane of the objective lens in TEM, its conjugate focal plane or the diffraction plane also possesses the same information on samples but presents in the form of reciprocal space. This is also quite useful to the researcher and allows them to study diffraction of electrons from samples to acquire the information on the phases present in materials. Another important optical element called “electron prism” which can be attached to a TEM and forms the basis for performing EELS in TEM instruments [13]. It can be attached either in column or post column of TEMs.

The object of this study presented in this report is to make list the advantages and limitations of a TEM analysis performed on nano-materials. This is accomplished by performing main TEM analyses of materials used in the field of nanotechnology. Such examples were deliberately taken from representative nano-materials having NPs below the size of 100 nm.

2. Experimental Methods

Altogether there are three microscopes of models Titan 60-300 ST from FEI Company (Hillsboro, OR) were employed to perform the TEM analyses of nano-materials. One of the utilized microscopes was equipped with an image corrector, the other one was equipped with a probe corrector, and while the third one was having no corrector of either type. Moreover all the TEMs were equipped with post-column energy filters or electron prisms of model GIF Tridiem 865 from Gatan Inc. (Pleasanton, CA). The most of datasets were acquired and processed in Gatan Microscopy Suite (GMS) of version GMS v1.85. Variety of TEM characterizations were performed on nano-materials suitable for a certain type of TEM analysis. For instance NPs with having sizes from 10 nm to single atoms were chosen for aberration corrected TEM (AC-TEM) and aberration corrected STEM (AC-STEM) analysis experiments. In both cases, the correctors were tuned prior to the experiments so that the co-efficient of spherical aberration (Cs) was measured to be below the value of negative one micron. AC-STEM and AC-STEM techniques were also applied to the imaging of silver NPs (Ag-NPs) below the size of 2 nm and tantalum (Ta) single atoms loaded on to nickel oxide (NiO) catalyst support, respectively. A carbon (C) nano composite containing oxidized iron cobalt NPs (FeCo-NPs) was included to perform the spectrum imaging (SI) in the STEM-EELS mode to generate the Fe and Co elemental maps. SI technique in the energy-filtered TEM (EFTEM) mode was applied to another material made up of C nano-fibers. Nano-fibers contained about 10 at.% of nitrogen (N) and were functionalized with TiO2 NPs. EFTEM-SI analysis was carried out by acquiring energy loss images by setting slit width of 5 eV and with a step of 5 eV as well. At the end a nano-composite material containing 2-3 nm size platinum (Pt) NPs loaded on to 20-25 nm size CeO2 NPs was selected for the ET analysis in the bright-field TEM (BF-TEM) mode. The main objective of the ET analysis was to investigate the loading of Pt NPs onto the CeO2 NPs. The ET analysis was carried out by tilting the specimens from -70° to +70° with an increment of 1° during the acquisition of datasets. The acquired ET datasets were then aligned and reconstructed with freely available software package IMOD to determine the loading of Pt-NPs on CeO2 NPs in three dimensions.
3. Results and discussion

3.1. Imaging of nano-materials

The focus was first turned to compare and contrast AC-STEM and AC-STEM techniques by carrying out the imaging of ~10 nm size Au-NPs. The corresponding results compiled by using these techniques are shown in Figure 1. It can be seen from there that in the low magnification range, the both techniques provide about similar quality information on the morphology of NPs. Furthermore both types of images can be used to determine the NP size distribution as well as for the determination of crystal structure. However, in higher magnification range, the situation changes a bit between AC-TEM and AC-STEM analyses of those 10 nm size Au-NPs. It can be seen by high resolution images of couple of NPs shown as inserts in Figure 1a and Figure 1b which were acquired with HR-TEM and HR-STEM techniques, respectively. There are a couple of important differences exist between those two images. First, it is the presence of no background in AC-STEM image as compared to BF-TEM. While the second difference is on quality of lattice fringe pattern, especially in the middle, exhibited by the NPs. It is apparent that mentioned lattice pattern in the HR-STEM image is of better quality as compared to image acquired with HR-TEM. The underlined differences between these techniques basically stem from different principles governing their image contrasts. It is well known that image-contrast in AC-TEM image is formed by the interference of transmitting electron waves through the NP and the observed interference pattern depends upon thickness of NP and difference of phases in the electron waves [10-11]. As a consequence the areas with different thickness can have a different interference pattern. It can be destructive on one place but can be constructive on another place. In spite of these difficulties, HR-TEM analysis of nano materials is a preferred way because of its ease and flexibility. On the other hand, the image-contrast in the STEM image of NP is not formed by the interference of transmitting electron waves and hence is less prone to changes in the thickness of NP. The lattice pattern in the image is a direct result of convolution of scanned sub-nanometer probe size with lattice columns.

![Figure 1](image.png)

Figure 1. Imaging analysis of Au-NPs with AC-TEM and AC-STEM. (A) BF-TEM image showing a uniform size Au-NPs and an inset of HR-TEM image of a single Au-NP. (B) DF-STEM image showing a uniform size Au-NPs and an inset of HR-STEM image of a single Au-NP.

The situation for realizing a successful TEM analysis changes dramatically for the imaging of NPs below the size of 2 nm to going down to single atoms. This is because during of the imaging of such small size NPs, the electron beam can also modify them. So special imaging conditions need to be
determined or established before achieving a successful imaging-analysis of such small size NPs. In this regard, the electron beam energy and mode of imaging are the most important parameters. Generally there is a specific range of parameters for certain type of samples. For instance, the lowering the accelerating voltage below 100 kV is a must for imaging of 2 dimensional materials as well as the imaging of NPs below the size of 2 nm in order to keep the beam-induced sample modification at the minimum level. Figure 2a contains an example of such analysis which is an aberration corrected electron micrograph of about 2 nm size Ag-NPs. The micrograph has been acquired by setting the image corrected microscope in BF-TEM mode at the accelerating voltage of 60 kV. It can be seen from there the Ag-NPs exhibit an excellent quality image contrast and further no beam damage was observed at this accelerating voltage. So it be stated that the underlined analysis enabled to determine the particle size distribution and crystal structure without causing any modification to NP size and shapes. The imaging of single atoms sitting on a 20-50 nm support is not that straightforward and requires completely different imaging conditions. This is because the convoluted image contrast of a single atom in the BF-TEM image is difficult to interpret and hence is prone to mistakes. Such subtleties can be avoided in certain cases by using the microscope in DF-STEM mode. This is particularly true for the cases when the atomic number (Z) of single atoms is quite different than that of support NPs or film. Figure 2b contains an aberration corrected DF-STEM micrograph of such a sample that was having Ta single atoms loaded on to ~10 nm size NiO support. This analysis not only allowed the imaging of Ta single atoms but it also enabled determining the population of Ta single atoms on NiO crystals.

![Figure 2](image.png)

**Figure 2.** Imaging of 2nm size NPs and single atoms. (a) Aberration corrected BF-TEM image showing a uniform size Ag-NPs. (b) Aberration corrected DF-STEM image of Ta single atoms on NiO support revealing a non-uniform decoration of NiO crystals with Ta atoms

### 3.2. Analytical electron microscopy of nano-materials

Another advantage of a TEM analysis is to enable having the spectroscopy analysis of samples at the spatial resolutions of nanometer to sub-nanometer range. The spectroscopy analysis can be accomplished in a couple of ways with a TEM namely the x-ray energy dispersive spectroscopy (EDS) and EELS. Both EDS and EELS spectroscopy methods have advantages and disadvantages over each other and are normally used as complementary techniques in a given TEM analysis. In spite of this, the EELS spectroscopy analysis is a preferred one when there exists the availability of both techniques because of its ability to provide both elemental and chemical information at the nanometer scale when
utilized along with DF-STEM mode. Figure 3 contains an example of such a STEM-EELS analysis that has been performed on a sample which was having a porous carbon (C) material functionalized with oxidized bimetallic FeCo-NPs. Such materials are promising candidates for the energy related applications [14]. It can be seen from Figure 3a that the oxidized FeCo-NPs were uniformly embedded in porous C material and while the corresponding EELS spectrum not only revealed the presence of all the expected elements in the sample but it also allowed the analysis of Fe-L23 and Co-L23 white lines to determine the oxidation states of both Fe and Co elements [13].

Figure 3. DF-STEM and EELS analysis of a porous C materials which has been functionalized with oxidized FeCo bimetallic NPs. (a) DF-STEM micrograph showing the average size of NPs was in the range of 30 nm. (b) Corresponding EELS spectrum revealing the presence of all four elements. Further, the analysis of Fe-L23 and Co-L23 white lines allowed determining the oxidation states of Fe and Co.

In addition to getting above mentioned useful information about the samples with STEM-EELS technique, high spatial resolution mapping of elements can also be accomplished by making the use of spectrum imaging (SI) method in this mode. The SI data sets were acquired in STEM-EELS mode first and then the acquired data sets were processed to generate the elemental maps having sub-nanometer spatial resolutions. Fe and Co maps of a couple of oxidized FeCo-NPs in Figure 3a are shown in Figure 4. It can be noticed from there that one of the NPs was a uniform alloy of Fe and Co and while the second NP was a having a core shell morphology. So it can be inferred from the presented results that such type of morphological information on NPs is essential for establishing an accurate structure-property relationship. Otherwise, by using results of conventional STEM-EELS analysis of Figure 3, it was possible to state that the FeCo-NPs were uniform in composition. It is to be noted that the elemental maps of several NPs of Figure 3 were generated in order to gather a statistics on the presence of uniform alloy and core shell NPs. In this way it was found out that there were about 40% NPs were possessing core shell morphology.
Carbon based nano fiber like materials are increasingly being utilized as a support for photo catalysis applications. Especially when these are functionalized with high band gap semiconductor oxides such as TiO$_2$. It is shown here next that such materials can be characterized at nano scales quite easily and accurately by using the TEM based techniques. For instance Figure 5 contains a BF-TEM micrograph along with a core-loss EELS spectrum from an empty region (or hole). It can be seen that the C nano fibers were functionalized with TiO$_2$ NPs quite uniformly as confirmed by a core-loss EELS spectrum of Figure 5(b) which has been from a region enclosed by a circle-1 in Figure 5(a).
Figure 5. Imaging and elemental composition of fiber-like carbon material that has been functionalized with TiO$_2$ NPs. (a) BF-TEM of TiO2 functionalized C-fibers that are supported by holey-carbon film. (b) A core-loss EELS spectrum from an area enclosed with circle-1 in (a) and it gives the elemental composition of functionalized fibers.

The intermixing of functionalized NPs with host materials like shown in Figure 5a is always a matter of concern and hence it is addressed next by using the EFTEM-SI technique. Figure 6 contains the results acquired with this technique. It was applied to a part of functionalized C nano fiber shown in Figure 6a which has been imaged with EFTEM mode to exhibit higher image contrast. The EFTEM generated elemental maps of all four elements namely C, N, Ti, and O are given in Figure 6b-e and then fat the end resultant Red-Green-Blue (RGB) composite of maps is given in Figure 6f. It can be clearly seen that the intermixing of TiO$_2$ NPs with C fiber was virtually non-existing and thus these fibers behave as only the carrier of TiO$_2$ NPs. In this way, the properties of TiO$_2$ NPs are not expected to change on these fibers and hence will retain their high efficiency for photo catalysis applications.

Figure 6. Elemental analysis of nano materials with EFTEM technique. (a) BF-TEM image of a TiO$_2$ functionalized nano fiber. (b) Elemental map of Ti generated with Ti-L23 edge. (c) Elemental map of O generated with O-K edge. (d) Elemental map of C generated with C-K edge. (e) Elemental map of N generated with N-K edge. (f) RGB Composite of all four elemental maps.
3.3. Three-dimensional imaging of nano materials with a TEM

It is important to remember that the TEM images are essentially two dimensional projections of three dimensional objects. As a consequence, the information about the third-dimension or along the penetrating electron-beam direction is suppressed and hence becomes difficult to find out about the sample properties in this direction. However it is becoming increasingly important in the field of nanotechnology to have information about NPs in all three dimensions in order to fully understand their properties [10-12]. Electron tomography (ET) in a TEM provides primarily provides just such type of three dimensional analysis at the nanometer scale lengths [15]. In ET method, first of all, the images of a sample at various angles are acquired by tilting it in small angular increments. The acquired stack of images is then aligned and back projected to have a three-dimensional volume or tomogram of the sample capable of revealing the three dimensional information about samples. Such analysis is particularly important for the characterization of catalytic materials which are sometimes functionalized with small size NPs [16]. Figure 5 contains the results acquired from the ET method applied to a material which was composed of CeO$_2$-NPs functionalized with Pt-NPs. The conventional BF-TEM image presented in Figure 7a is basically used as a control for the ET analysis. It is a projection image and hence contains some places where the presence of Pt-NPs along with CeO$_2$-NPs cannot be easily established. For instance, the four places marked with four circles have been selected in Figure 7a to underline this point. Interestingly but expectedly the three volume-slices from the different region of tomogram of Figure 7a revealed that not only all those four encircled places have Pt-NPs but were found to be lying at different height levels. The presence of Pt-NPs at different height levels in tomogram is corroborated by the given volume-slices in Figure 7b-d where it can be seen that the Pt-NPs appeared in encircled areas in different slices. So it is suffice to say that the ET analysis is essential to fully characterize the loading of small size NP onto large size support NPs.

**Figure 7.** ET analysis of CeO$_2$ and Pt NPs. (a) BF-TEM projection image of sample at 0° angle. There are few ambiguous places in it where the presence of Pt NPs does not seem to be an obvious thing. (b) The volume slice from the bottom part of the area revealing that the place enclosed with circle 1 indeed had Pt NPs. (c) & (d) Similarly the middle and top slices revealing the presence of Pt NPs at the remaining three places highlighted in (a).
4. Conclusions
In the light of presented TEM analyses of different nano materials, it can be stated with confidence that TEM offers a comprehensive recipe of their characterization. Specifically both the AC-TEM and AC-STEM techniques can be employed to image materials comprised of single atoms to small size NPs. Though a suitable electron beam conditions should be adapted for the imaging of materials having NPs of size 5 nm or close. In other words for the imaging of atom clusters, the electron energy of 100 keV or less should be used during the analysis. While AC-STEM mode is quite suitable for the imaging of high atomic number single atoms sitting on different support NPs. For the analytical characterization of nano materials, both STEM-EELS and EFTEMSI techniques can be employed in determining the elemental distributions in NPs. STEM EELS technique offers composition and distribution of elements in NPs with spatial resolution below the size of one nanometer. However its datasets are acquired in the sequential manner and thus it takes generally several minutes in completing the acquisition of datasets. On the other hand, EFTEM SI technique offer the same elemental analysis of nano materials but its datasets generally possess spatial resolution worse than one nanometer. However, unlike STEM EELS, EFTEM SI it a parallel data acquisition and hence offers the completion of datasets normally in just few seconds. At last but certainly not least, the ET analysis allows determining three dimensional analysis of nano materials at the nanometer scales and can be useful in investigating the loading of small size NPs onto larger size host NPs.

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6. References
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