Maintaining the genuine structure of 2D materials and catalytic nanoparticles at atomic resolution.

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Keywords

Abstract:

The recent development of atomic resolution, low dose-rate electron microscopy allows investigating 2D materials as well as catalytic nano particles without compromising their structural integrity. For graphene and a variety of nanoparticle compositions, it is shown that a critical dose rate exists of $< 100 \text{ e}/\text{\AA}^2\text{s}$ at 80 keV of electron acceleration that allows maintaining the genuine object structures including their surfaces and edges even if particles are only 3 nm large or smaller. Moreover, it is demonstrated that electron beam-induced phonon excitation from outside the field of view contributes to a contrast degradation in recorded images. These degradation effects can be eliminated by delivering electrons onto the imaged area, only, by using a Nilsonian illumination scheme in combination with a suitable aperture at the electron gun/monochromator assembly.

Introduction

Nanoparticles are interesting for many different fields of application. Normally consisting of a few nanometers (> 5 nm), their properties depend on their size, shape and atomic distribution in volume and surface. Their physical and chemical properties are different from those of the bulk. Their crystal structure and atomic distribution account for such differences. Additionally, applications such as catalysis require knowledge of the atomic distribution on the particle surface as a function of size and shape in order to understand the mechanisms that promote specific chemical reactions. It is thus of importance to use electron microscopy methods that ensure their stability and integrity under the electron beam. Structural rearrangements of the surface or volume of nanoparticles under the electron beam are therefore unwanted. They must be considered, especially in order to have the beam sample interaction under strict control.

Nanoparticle synthesis has had a considerable development in recent years. Interestingly, a great wealth of core shell designs or simply a desired coverage of a given core that promote desired chemical reactions have been proposed in order to produce cost effective, selective and efficient catalysts. Core –shell, noble metal free as well as shape selected catalysts are specially important for the development of fuel cells and other energy devices [1]. Such a relevant advance in materials synthesis calls for materials characterization with atomic resolution. Certainly, a rich body of literature on the characterization of nanoparticles by TEM (Transmission Electron Microscopy) and STEM (Scanning Transmission Electron Microscopy) in high resolution modes, Z contrast or even imaging spectroscopy reveals precise shapes and atom distribution in catalysts [2-5]. In many cases the investigated nanoparticles show regular shapes that one expects if crystal growth is performed close to thermodynamic equilibrium that, however, cannot be taken for granted. By comparison, investigations only emerge that consider possible structure alterations during the observation of materials by the highly energetic electron beam [6-10]. In some cases, catalysis research is made after a proper thermal stabilization of the nanoparticles [11]. Commonly, however, the microscopic sample characterization takes place right after synthesis and is used to interpret a variety of electrochemical results.

Modern current electron microscopes are able to extend spatial resolution to subÅngstrom values due to aberration correction. There is little doubt that for many

years the goal of electron microscopy has been to increase spatial resolution. Nevertheless once this has been reached to the maximum possible physical limit, research needs to consider other important factors. Stability of the electron beam, beam sample interaction and possible dynamics of specific mechanisms can make electron microscopy more useful than ever.

On the other hand, it is well established that electron beam-sample interactions can give rise to sample alterations [12, 13]. In addition, it is pointed out that they are most critical when dealing with particles of small dimensions due to their markedly large sensitivity [14, 15]. In a high resolution mode, it is common practice to describe beam-sample interactions by mainly two mechanisms i.e., knock-on damage (sputtering) and radiolysis [12, 13]. Sputtering is likely to appear at high accelerating voltages while bond fracture has been observed at relatively lower energies and especially for polymers and other materials containing hydrogen bonds. Nevertheless, early reports by Smith et al. [14] already point out the possibility that sample heating during observation occurs since they find a dependence of the sample structures on the current density of the incident beam and the degree of contact between particle and substrate. Indeed it has been recently highlighted that a control of dose rates is of prime importance [16, 17]. Consider for example literature reports on detecting amorphous nanoparticles [5, 18,19]. Certainly, it is very feasible that such particles are truly amorphous. However, a modern field-emission transmission electron microscope (TEM), operating at an accelerating voltage between 20 and 300 keV, can produce high current densities that only few materials can survive without being damaged [13, 19]. Therefore, it is a priory not clear whether or not such particles are genuine amorphous or if small particles turned amorphous during their observation with high energetic electrons unless critical irradiation parameters are determined that guaranty maintaining structural integrity.

This contribution addresses critical dose rates for graphene and small particles that have been synthesized for catalyzing energy-related chemical reactions. In both cases, low dose electron microscopy is applied and compared to higher dose conditions. An attempt is done to show that the applied method considers as many parameters as possible in order to control the beam-sample interaction and maintain it within the limits given by a negligible transformation of the sample, i.e., limit atom motion in

the sample as a consequence of the incoming beam. In all cases, an effort is made to still achieve atomic resolution.

Experimental Procedures

The TEAM 0.5 microscope is used to perform all experiments described in this investigation. The TEAM 0.5 microscope is the product of a special development that can provide a spatial resolution below 0.06 nm. Variation of the electron dose can be made by using the monochromator settings to displace the beam and the monochromator slit. It has a high brightness gun that can produce high current densities in the 10^6 A/m^2 range at 300 keV of accelerating voltage. In this work, the TEAM 0.5 microscope is used in TEM mode with the monochromator excited to provide an energy spread of 0.1 eV for imaging. The microscope is used at 80 keV where the maximum current density lies in the $3\text{-}5 \times 10^5 \text{ A/m}^2$. This is equivalent to 20-25,000 counts per second (cps) for a sampling rate around 0.015 nm/Pixel at a magnification of around 450 kx. However by displacing the beam with the monochromator settings, it is possible to decrease the dose rate to 10-20 cps and reach a current density of around 5-10 [attoA/Å²s i.e. 500 A/m²s](#), in a matter of seconds. This represents a huge current decrease that involves rather noisy experimental images. Additionally the use of the monochromator slit reduces the area for beam sample interaction giving rise to a good thermal stability. The TEAM 0.5 microscope is very stable regarding the setting and correction of aberrations i.e., C5, C3, A1, A2 and A3 can be set used confidently over periods of time sufficiently long to take focal series. In this investigation, focal series of 40 images are used in order to perform an exit wave reconstruction procedure with them and the software MacTempas ®. Such a procedure renders both phase and amplitude images that can still be finely tuned to correct for remaining aberrations. The use of MacTempas ® allows determining the accuracy of the reconstruction procedure both as the focal series is used and from the final amplitude and phase images. In this procedure, alignment of images is critical. Especially in the case of graphene, images become quite noisy and the alignment procedure requires the use of cross correlation which renders a high accuracy that is sufficient to confidently image dumbbells with a distance of separation around 0.14 nm). No filtering of these images is given.

The samples that are used in this investigation are graphene, both as multi and monolayered material as well as nanoparticles produced by soft chemistry methods. Nanoparticles made of Pd, PdCu, Pd₅Cu₄Pt, and NiO@Pt (core-incomplete shell structure) are investigated. Their synthesis method is given elsewhere [20, 21]. All of these nanoparticles are used for energy devices, some of them for fuel cells [20, 21] and others as part of solar cells to transform solar energy into a fuel.

Results and Discussion

Graphene is a material with a light element structure rather sensitive to the beam. There are several experimental observations showing atomic resolution at 300 keV and 80 keV in both STEM and TEM modes [22-24]. However, in this investigation the effect of the electron dose rate is exclusively examined. Figure 1 shows experimental images taken at different focal settings for a dose rate of $60 \text{ e}^-/\text{\AA}^2\text{s}$ (i.e., $9.5 \text{ attoA}/\text{\AA}^2\text{s}$ or $950 \text{ A}/\text{m}^2\text{s}$) in average. The accelerating voltage is 80 keV and 1 s of exposure time. Depending on the defocus, some broad features can still be noticed but most details of the structure are hidden. Nevertheless, the corresponding Fourier transforms do show crystalline reflections up to $1.2 \text{ \AA}$ as can be seen in Fig. 1d. A total of 40 images are used for exit wave reconstruction with a starting defocus of 16 nm and the final one at -23 nm with a step ΔF of 1 nm. In the exit wave reconstruction procedure, alignment of images is critical. [Since images become quite noisy, the alignment procedure requires the use of cross correlation which renders a high accuracy which is sufficient to confidently image dumbbells with a distance of separation around 0.14 nm\). No filtering of these images is given.](#) The reconstructed amplitude and phase images are given in Fig. 2a-b, respectively. A monolayer, double layer and a triple layer can be identified. Because of the low dose imaging, the monolayer shows a relatively low contrast but the atom positions can be still recognized. Noteworthy, the rim of the monolayer can be readily interpreted in most of its sections. As for the surrounding triple layer, all the expected variations of intensity are found as can be seen by comparing to the corresponding simulation (Fig. 2d). Figure 3a shows a magnified view of the phase image from the vacuum and monolayer area. Figure 3c also shows intensity line profiles taken from the monolayer and across the characteristic dumbbells in the graphene structure, [the exact location is given in Fig. 3b.](#) As can be seen, the contrast accounts for values close to 50% for the

observation of the dumbbells in the graphene structure. This is a considerable improvement with respect to direct images taken in high dose in the same microscope [22] but lower than phase images taken in high dose conditions [23]. This can be expected due to the conditions in use in [23]. For instance, a higher magnification has been also used which in turn enhances the signal strength because of the present signal damping by the modulation transfer function of the camera. Nevertheless there is a significant improvement in Fig. 3 with respect to previous reports (see Fig. 4 in [23]). There are no ghost-like atom images in the low dose results i.e. a complete absence of carbon atom displacements at the vacuum/single layer interface in images recorded with low dose rates. Even with the current relatively lower contrast, it is sufficiently high as to follow the atomic positions around the vacuum in the single layer region. This is done in Fig. 3b where circles are added in order to schematically show the atom positions in the monolayer. This happens as well in the zones where the triple and the single layers meet, zig-zag and arm chair atom configurations can be easily distinguished.

These configurations are stable atomic positions that have not been affected by interaction with the electron beam due to the considerable reduction of the total beam current per unit time in this low dose approach. The use of higher dose rates at similar accelerating voltage, implies taking experimental images that register a given moment in time of a continuously changing atomic arrangement. In high dose rate mode, atom displacement gives rise to a great deal of atom motion at an accelerating voltage of 80 keV in graphene. In such conditions acquisition of a focal series produces images with atoms in some layers that have disappeared in the following ones and ghost images in the reconstructed phase image. Thus the phase images shown in Figs. 2-3 are actual atom configurations that have remained stable and undisturbed by the electron beam. Figure 3 shows the edge configurations in the phase image, retained for as long as the experiment has been performed (around 2 min). This can hardly be achieved under high dose rate conditions where a lot of activity, most likely sputtering can be seen at 80 keV. Apparently all atom sputtering is stopped as soon as the dose rate drops below a value around $80 \text{ e}^-/\text{\AA}^2\text{s}$ at the accelerating voltage in use.

The need to use a monochromator slit in low dose imaging is made evident in Fig. 4. It reduces image width. The slit effectively reduces the illuminated sample area and

thus the sample beam interaction. While sputtering and radiolysis can hardly change by reducing the area of interaction, sample heating can most likely be affected in such circumstances. Figure 5 shows schematically the position of the slit with respect to the monochromated beam, clearly the beam exposed area decreases considerably. As indicated, the magnification is selected to approximately have an illuminated area that coincides with the observed camera window. As for Fig. 4, the images have been acquired with a higher dose ($9,500 \text{ e}^-/\text{\AA}^2\text{s}$) in order to show the effect directly with experimental data. Fig. 4a is an image taken with the use of the monochromator slit while Fig. 4b presents a similar image but acquired by having the complete monochromated beam reaching the sample, no slit is in use. There are small differences in the images since they have been taken at an interval of around 1 min. This is a sufficiently long time for the beam to promote atom activity and as a result, holes have slightly different sizes. Nevertheless the most important difference has to do with image width of the different features. This is qualitatively clearer in the case of hole rims and broad variations of contrast but definitely present also in the rest of the image features. Arrows are added in both images to show some of the broad features to consider. Contrast degradation can also be seen in the atomic structure of the samples. Figs. 6 a,b show line profiles that measure the recorded intensity as a function of position along dumbbell directions in the graphene monolayer. There is a clear broadening of the image when the monochromator slit is absent as well as a considerable contrast decrease. The contrast measurement produces values between 20 and 30 % for the phase image without the monochromator slit and between 45 and 55 % when the slit is in use. Figure 7 shows a series of images taken successively at short intervals from the same region with and without the use of the monochromator slit. The effects shown in Fig. 6 are repeated and most importantly, it can be shown that they are completely reproducible and that other factors (focusing changes, aberrations, microscope instability, etc.) are not involved. Thus, it is demonstrated that electron beam-induced phonon excitation from outside the field of view contribute to a contrast degradation in recorded images. Such a degradation effects can be mitigated by delivering electrons onto the imaged area, only, by using a Nilsonian illumination scheme in combination with a suitable aperture at the electron gun/monochromator assembly. On the other hand, [the dumbbell separation in graphene is only affected when the intensity of the individual columns becomes broad enough to reach the Sparrow resolution limit \[25\]. In such a case, each peak location](#)

can be affected due to the involved intensity convolution and thus the measurement of the dumbbell separation becomes different. As for the present observations, in cases where no slit is used the contrast difference is smaller and peaks are broader, thus locating the intensity peak becomes more difficult and subject to a larger statistical variation of the measurement. Clearly using a low dose rate helps reducing peak broadening and provides a means to make a more accurate measurement of the dumbbell distance in the case of graphene and in general.

Observation of nanoparticles requires control on the electron dose in order to avoid transformation of their crystalline structure and atomic distribution. In applications such as catalysis, the atomic distribution at the particle surface is extraordinarily important and needs to be preserved from any beam induced variation. Figures 8-10 show experimental and phase images of nanoparticles in the systems Pd, CuPd and Pd₄Cu₅Pt that have been used as catalysts (oxygen reduction) in polymer electrolyte membrane (PEM) fuel cells [20]. Cu-Pd nanoparticles are chemically synthesized as powders and Fig. 8 shows a typical example of the experimental focal series that are used to apply the exit wave reconstruction (EWR) procedure. These images are taken with a dose rate of approximately $100 \text{ e}^-/\text{\AA}^2\text{s}$ and have been arranged from positive (+15.4 nm) to negative (- 27.5 nm) defocus as indicated. The focus variation (approximately 1 nm) can easily be followed by analyzing the Fresnel fringes at the particle-vacuum interface and from the minimum contrast condition (frame 14 in Fig. 8) a correct starting defocus value can be assigned in the corresponding software. As expected images close to Scherzer focus (frames 8 - 10) show a great resemblance to the results of exit wave reconstruction (phase image) as far as contrast is concerned. As shown in Fig. 8, experimental images do show a considerable contrast and as expected, great differences. Figure 9 shows the result of the EWR procedure i.e., the corresponding phase image and using a slightly larger section of the experimental image. There are several atom large steps along the surface that suggest little to none surface reconstruction and thus a shape that deviates from thermodynamical equilibrium considerably. Additionally, the phase intensity has variations that can be better appreciated in thinner regions of the ensemble. Arrows are added to indicate the atomic columns for the intensity measurements shown in Fig. 9 b-d. In the case of the thinner sections (arrows 1 and 2), the measurements show the expected intensity variation for a tridimensional shape if one assumes that atom columns near the edge

contain fewer atoms than those in the middle of the particle. However this expectation is broken at specific atomic columns most likely as a result of the compositional variation in the CuPd solid solution. Intensity measurement in thicker regions (see arrow 3) show a flat profile with slight variations suggesting the random distribution of Cu and Pd atoms in the atomic columns and the variation of the specimen thickness. These observations can only be found due to the slight beam sample interaction that the low electron dose rate, in use, promotes.

Phase images after EWR of Pd, Cu-Pd and Pd₄Cu₅Pt nanoparticles are given in Fig 10. This series of catalysts have been tested in PEM (polymer electrolyte membrane) fuel cells for the oxygen reduction reaction (ORR) in acid medium with encouraging results in order to reduce the amount of Pt in use [20]. The experimental images are taken with an electron dose rate between 75 and 150 e⁻/Å²s as indicated. In general all phase images show little to no beam interaction effects. In the case of Pd particles (Fig. 10a, dose rate 75 e⁻/Å²s) relatively larger particles are synthesized and form conglomerates but still it is possible to image those bordering the ensemble. The phase images have intensity maxima with rather homogeneous intensity and varying proportionally to the column thickness, according to a regular ellipsoidal shape. The particle surface is covered by a thin amorphous layer, which can be traced back to the corresponding experimental images. This layer is not continuous and some parts of the nanoparticles appear to be completely free of such foreign atoms. There are also atomic steps along the particle surface i.e., little surface reconstruction has taken place. Some of them have been pointed out by means of arrows. Figure 10b shows a magnified view of the phase image of a CuPd nanoparticle in Figure 9. The phase images in Figure 10 c-d are obtained from nanoparticles with a nominal composition of Pd₄Cu₅Pt and a dose rate of 120 and 150 e⁻/Å²s, respectively. Two size classes are selected in this report to test whether or not the particle volume plays a role in the beam sample interaction once the dose rate is decreased. The smaller nanoparticle is completely isolated and thus in conditions of rather poor heat conduction but still the phase image shows all of the characteristics of atomic resolution together with strained lattice planes, little to none surface reconstruction, a relatively thick amorphous layer and varying atomic column intensities that most likely correspond to the nature of the atomic species in a given column i.e., the atomic column composition. This will be addressed in a forthcoming publication in more detail. X

ray diffraction has shown that the amorphous component is present due to the chemical agents necessary for the synthesis procedure [21]

NiO nanoparticles are catalysts that can be used in fuel cells and solar fuel cells. Figure 11 shows phase images of a NiO nanoparticle with a shell coverage of 8 at.% Pt. A core-incomplete shell structure is the objective of the synthesis procedure for a solar cell component with a considerable reduction in the Pt content. The experimental images (40) in the focal series have been taken by using a dose rate of $56 \text{ e}^-/\text{\AA}^2\text{s}$. The reconstructed exit wave function is given in Fig. 11a together with the corresponding diffraction pattern (Fig. 11b). This is obtained by applying a Fourier transform to the wave function. The arrow points out a reflection typical of the spinel structure for the nickel oxide. The phase image is shown in Fig. 11c. The nanoparticle has an irregular shape with some tendency to form facets parallel to cube and octahedral planes in the cubic crystalline structure (spinel) but still with several atoms out of position from the expected regular polyhedral shape. Then it is to expect that the interaction with the beam is negligible and insufficient to alter neither the chemical distribution of atomic species nor the as synthesized crystallographic structure of the nanoparticles. Additionally the crystallographic planes are bent as has been shown already for similar instances. Figure 11 also shows a comparison of phase images that have been obtained by using different sets of experimental images in the focal series. They are all identical regardless of whether the first/last 20 images (Figs. 11 d-e, respectively) or the whole 40 images of the series (Fig. 11c) are used for the exit wave reconstruction procedure. This implies that the nanoparticle has hardly suffered any alteration by beam interaction for the dose rate in use despite being completely isolated and subject to beam heating.

Sample-beam interaction is a key issue in aberration corrected electron microscopy. Nevertheless the need to have a well aligned equipment as well as to perform a satisfactory aberration correction, are prerequisites of a meaningful experimental observation. The TEAM 05 together with the procedure to reconstruct the exit wave, allow for both the use of finely tuned equipment with the possibility to correct residual aberrations. Figure 12 shows the amplitude image of the NiO@Pt nanoparticles analyzed in Fig. 11 together with an enlargement of the central zone. The dark ring surrounding the intensity maxima in the amplitude image is an

indication of the quality of the aberration correction. In the present case, the diameter of this ring is 0.08 nm and gives a measure of [a perfect aberration correction up to this spatial limit](#). Accordingly the exit wave reconstruction procedure can be used over time to obtain a measure of the stability of the microscope. Fig. 12 also shows the time variation of two fold astigmatism and coma for the TEAM 05. The equipment is sensibly stable over the required period of time for most EWR procedures and thus the aberration correction is reliable.

Nanoparticles can be affected by rather low electron doses. For instance, it is necessary to reduce this parameter below $60 \text{ e}^-/\text{\AA}^2\text{s}$ for the case of NiO nanoparticles and below $70 \text{ e}^-/\text{\AA}^2\text{s}$ for graphene. Figure 13 shows phase images of a beam induced transformation in a NiO@Pt nanoparticle with an 8 at. % Pt coverage. First, a low dose is used ($55 \text{ e}^-/\text{\AA}^2\text{s}$) and the corresponding phase image (Fig. 13a) shows an irregularly shaped nanoparticle with intensity variations from column to column similar to above Fig 11c (identical batch and sample). When a relatively higher dose is used to acquire the focal series ($300 \text{ e}^-/\text{\AA}^2\text{s}$), clear transformations take place that produce the phase image shown in Fig. 13b. Both the shape and the atomic distribution change i.e., now a roughly spherical nanoparticle can be seen with a crystalline arrangement that involves large orientation differences that prevent imaging the whole particle. Since a round shape involves a lower surface energy, clearly the particle beam interaction drives the dynamics of the shape change as expected for a temperature increase i.e., the shape change (and corresponding atomic motion) can be directly related to particle heating. Further atomic motion can also be inferred from the phase image in Fig. 13c. This is obtained after acquiring a 40 image focal series with a dose rate of $1400 \text{ e}^-/\text{\AA}^2\text{s}$ in approximately 2 min. The originally monocrystalline particle has transformed and becomes a bicrystal. As can be seen, this particle is originally isolated and the transformation can only be due to heating by the beam as the dose rate becomes sufficiently high.

The current density per unit time on the sample is a decisive parameter on the sample beam interaction mechanisms. Control of this factor is then of prime importance. There have been efforts to reduce the incident beam energy of aberration corrected electron microscopes [26]. However changing the wavelength of the incoming electrons without reducing the number of them reaching the sample per unit time has

a lower influence on the beam sample mechanisms of interaction [14, 16]. Thus reducing the dose rate becomes an interesting field of research and especially for sensitive samples and nanomaterials. Some materials are rather sensitive to the electron beam. Graphene is a typical example of a 2D, low Z (atomic number) material that for electron energies above 80 keV shows a moderate to high susceptibility to knock on or sputtering damage. Atoms are detached from the sample and within seconds, there is a visually changing structure i.e., as a focal series is acquired [23] the rim of the sample changes, giving rise to “ghost” atom images with lower intensities. This is also true for semiconducting materials either in thin films, as quantum wells or as nanoparticles or quantum dots (GaInN, GaIn, Cd-Se, etc), they are rather sensitive to the beam also due to knock on mechanisms. Defect formation, deformation and bending are clear signs of such an interaction that most likely alter the atomic distribution in the samples [27-29]. As the electron energy is reduced, the general expectation has been to reduce the beam interaction but at least with graphene, that is not achieved because then radiolysis takes place (beam energy < 20 keV) and material is removed from the sample also at a rapid rate [30]. Using a slightly higher energy [40 keV] has proved to be successful [27] for the observation of graphene and other nanomaterials. Nevertheless, results shown in this investigation for 80 keV and low dose rate confirm the general trend and higher impact of reducing the beam current as compared to the beam energy. As for nanomaterials, the interaction between the beam and the sample often translates into lattice vibrations or heat as above shown. Thus high-resolution images can deteriorate if recorded in high dose conditions due to a transformation of the isolated nanoblock.

Concluding remarks

Low dose rate electron microscopy is used in graphene (weak scattering material) to recover phase images in an EWR procedure with atomic resolution. The corresponding phase images show stable atomic configurations at the vacuum-monolayer interface as well as between thickness layers with sufficient contrast as to recognize single atom positions. No artifacts are produced by the EWR procedure mainly due to the stability of the material during data acquisition. The use of a monochromator slit reduces vibration of the sample considerably. This is interpreted in terms of phonon excitation from outside the field of view that normally contributes

to contrast degradation. The use of the slit clearly mitigates such contrast degradation effects.

Nanoparticles are successfully imaged with a low dose rate, the obtained phase images have atomic resolution. There is no alteration of the nanoparticle crystalline structure or chemical distribution when dose rates under $100 \text{ e}^-/\text{\AA}^2\text{s}$ are used. Besides atomic resolution, low dose rates ($< 100 \text{ e}^-/\text{\AA}^2\text{s}$) typically allow for imaging of atomic steps along nanoparticles surfaces, complete or incomplete layers of amorphous materials around as synthesized nanoparticles, bent lattice planes and shapes that deviate from equilibrium. Higher dose rates (300 and $1400 \text{ e}^-/\text{\AA}^2\text{s}$) produce transformation of isolated nanoparticles in relatively short times that become apparent through shape changes and atom redistribution.

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Figure Captions

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