# Diffraction microscopy using 20 kV electron beam for multiwall carbon nanotubes

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Diffraction microscopy with iterative phase retrieval using a 20 kV electron beam was carried out to explore the possibility of high-resolution imaging for radiation-sensitive materials. Fine, homogeneous, and isolated multiwall carbon nanotubes (MWCNTs) were used as specimens. To avoid lens aberrations, the diffraction patterns were recorded without a postspecimen lens. One- and two-dimensional iterative phase retrievals were executed. Images reconstructed from the diffraction pattern alone showed a characteristic structure of MWCNTs with the finest feature corresponding to a carbon wall spacing of 0.34 nm. 
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Low-damage imaging with high resolution and high contrast is required for radiation-sensitive materials, for example, biological samples or carbon materials. In paticular, in the case of carbon nanomaterials, their physical characteristics (e.g., electrical properties of nanotubes) are closely linked to their atomic structures. High-voltage electron microscopes (more than 100 kV) are mainly used to analyze such structures, but they often cause specimen damage due to electron radiation. Low contrast due to low scattering of nonperiodic light elements is also a problem. Relatively low-energy electron microscopes with an acceleration voltage of a few tens of kilovolts are often used to observe radiation-sensitive materials because of low knock-on damage and high contrast with large cross section. However, their resolutions are not fine enough to elucidate atomic-scale structures.

Meanwhile, diffraction microscopy with iterative phase retrieval[1,2] is one of the most promising techniques for high-resolution imaging. Using this method, the structure of an object can be reconstructed from diffraction intensities by retrieving phases via an iteration procedure, avoiding lens aberrations and instrumental instability. Iterative phase retrieval has primarily been applied to x-ray beams[3–5] with a highly coherent x-ray source. In contrast, there are few results on iterative phase retrieval with electron beams. Weierstall *et al.*[6] reported the reconstruction of a double-hole image with resolution of about 5 nm using an electron beam with a 40 kV acceleration voltage and Zuo *et al.*[7] reported high-resolution imaging with 0.1 nm resolution at 200 kV using a double-wall carbon nanotube.

To explore high-resolution imaging with a relatively low-energy electron beam and verify the practical use of diffraction microscopy, we adopted iterative phase retrieval for a 20 kV electron beam diffraction pattern. A schematic ray diagram of our experimental instrument is shown in Fig. 1. The electron beam, emitted from a thermal-field-emission gun, is focused on a specimen by a magnetic lens. The geometrical convergence angle on the specimen is determined by the ratio between the radius of the aperture installed in the magnetic lens and the distance between the aperture and the specimen. In this experiment, because the aperture radius was set to 5 $\mu$m and the aperture-specimen distance was about 100 mm, the geometrical convergence angle was about 0.05 mrad. A diffraction pattern was recorded on the imaging plate without a postspecimen lens (i.e., without projecting the back focal plane of an objective lens) with a camera length of 570 (±5) nm.

Multiwall carbon nanotubes (MWCNTs) grown by arc discharge were used as specimens. Crushed CNT chunks, sprinkled on a Cu mesh (2000) for a transmission electron microscope (TEM), were used. Beforehand, these chunks were observed in an HF-2000 TEM (Hitachi High-Technologies Corporation) at 200 kV, and fine, homogeneous, and isolated MWCNTs were selected for the experiment.

A diffraction pattern of $2048 \times 2048$ pixels, obtained using the experimental instrument with a 20 kV acceleration voltage, is shown in Fig. 2(a). The exposure time was 60 s. Because the diffraction pattern after exposure was not greatly changed, we think that the structure of the CNT was not significantly affected by the electron beam radiation. To reconstruct the object image, this diffraction pattern was applied in the iteration procedures, which retrieve phases by iterating Fourier transforms with constraints in reciprocal and object space.[1,2] As a constraint in reciprocal space, the square root of the diffraction intensity was used for the amplitude. From the diffraction pattern in Fig. 2(a), data corresponding to the central $77 \times 24$ pixel area were removed to avoid the effect of intensity saturation around a strong central beam. The calculated amplitude during the iteration was applied to fill the removed missing data. In this sense, our reconstructions were processed from the diffraction pattern alone (i.e., without using a Fourier transform of the object image to recover missing information). In object space, a rectangular area of $70 \times 2200$ pixels was adopted as a constraint, namely a support. For the iteration procedure, we applied a combined algorithm based on hybrid input-output

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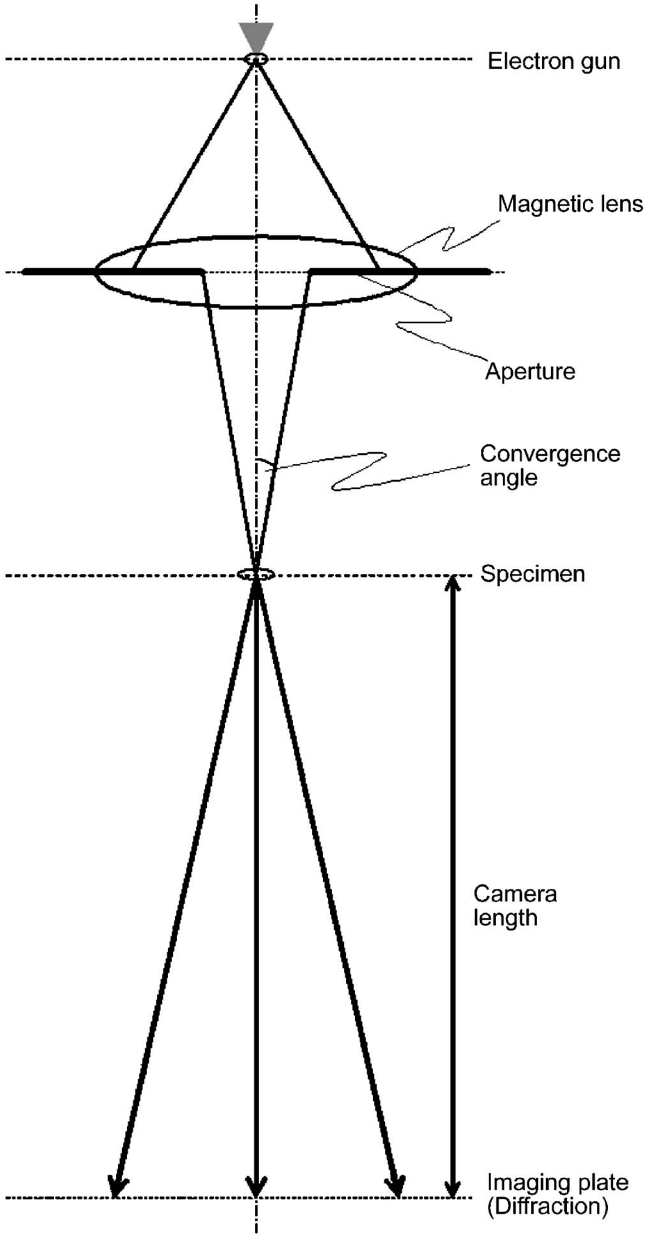


FIG. 1. Schematic ray diagram of our experimental instrument (not to scale).

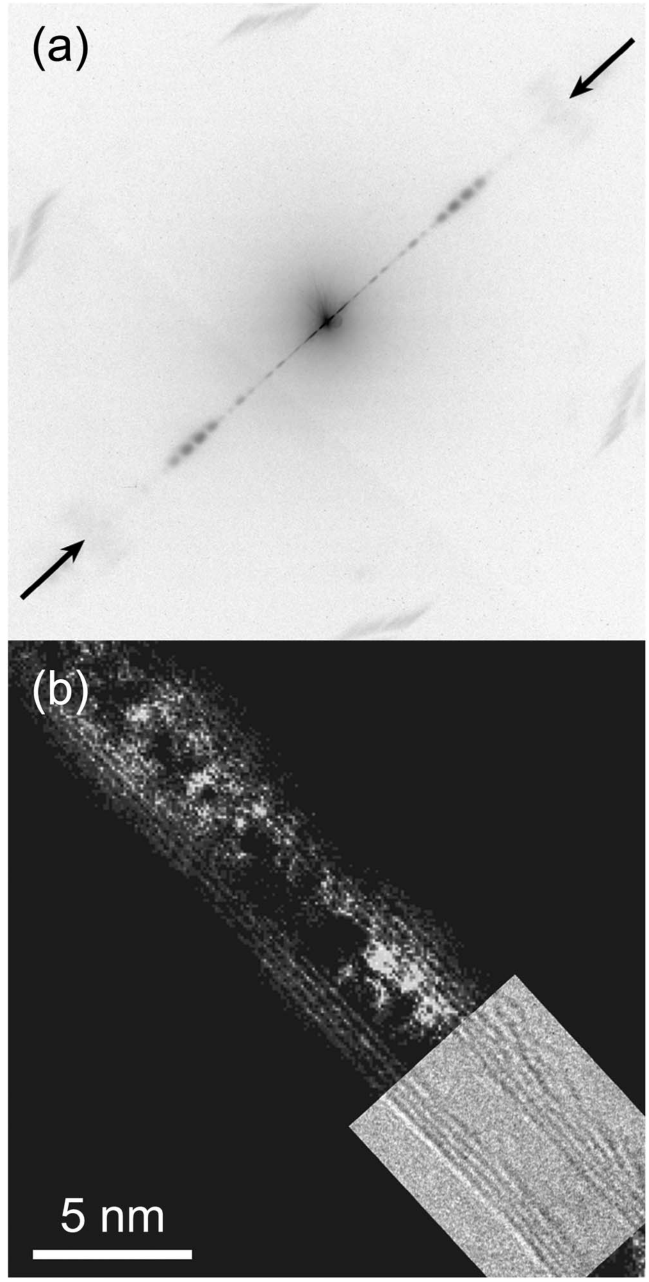


FIG. 2. (a) Reversed diffraction pattern of MWCNT using 20 kV electron beam and (b) result of two-dimensional phase retrieval. TEM image with the same magnification is shown in the inset.

(HIO) with error reduction (ER).[2] An $R$ factor was used to monitor the progress of the algorithm in the iteration procedure.[7]

In two-dimensional phase retrieval, 500 iteration HIO with $\beta$ of 0.5 and 500 iteration ER algorithms were processed. Based on the camera length, number of pixels, and pixel size, the pixel size of the image and the field of view in the reconstructed object space were estimated to be 0.0956 and 196 nm, respectively. The reconstructed object image from the experimental diffraction pattern alone is depicted in Fig. 2(b), which was extracted from the $2048 \times 2048$ pixel overall field of view. Also inserted in the figure is a TEM image of the specimen with the same magnification. The TEM image shows the outer and inner diameters of the MWCNT, which are 4.0 (±0.3) and 1.9 (±0.3) nm, respectively, with four walls. In comparison with the TEM image, the reconstructed image shows the characteristic structure of the specimen, in which the inner and outer diameters and spacing of the walls almost coincide.

To analyze the results of phase retrieval quantitatively, we also processed one-dimensional phase retrieval because the characteristic structures of MWCNTs are reflected mainly in a one-dimensional streak in a diffraction pattern [arrows in Fig. 2(a)]. A one-dimensional profile of the diffraction intensity is shown in Fig. 3(a) on a log scale. From the data in Fig. 3(a), the central 77 pixels were removed to avoid the effect of intensity saturation. The same method as in the two-dimensional procedure was used to fill in the removed data. In this iteration procedure, the support size was set to 70 pixels. Figure 3(b) shows a reconstructed profile from one-dimensional phase retrieval with 500 iteration HIO ($\beta$=0.5) and 500 iteration ER algorithms. In Fig. 3(b), eight sharp peaks can be seen. From these peaks, the inner and outer diameters of the MWCNT can be estimated at 40 (±1) pixels and 20 (±1) pixels, which correspond to 3.8

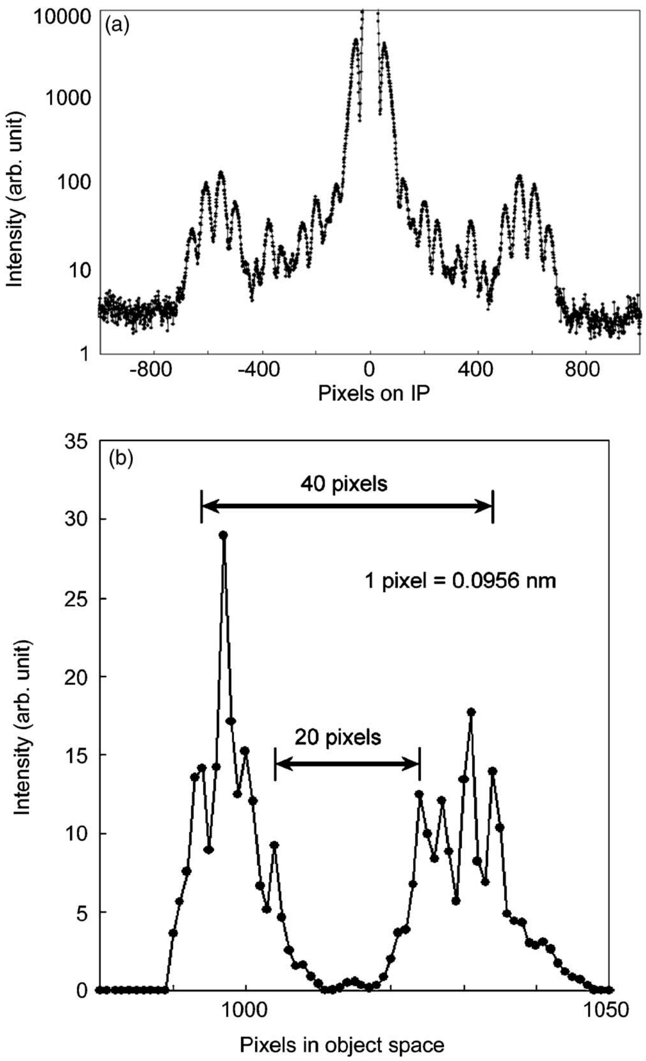


FIG. 3. (a) One-dimensional profile of diffraction intensity on a log scale with an acceleration voltage of 20 kV and (b) intensity profile in object space resulting in one-dimensional phase retrieval.

(±0.1) and 1.9 (±0.1) nm, respectively. The spacing between small peaks ranges from 3 to 4 pixels, which corresponds to a carbon wall spacing of 0.34 nm (actually, 3.5 pixels). In this one-dimensional reconstructed profile, the spacing of carbon walls as well as the inner and outer diameters agree with the values measured in the TEM image. From this result, we can conclude that our one-dimensional phase retrieval reconstructs the characteristic structure of MWCNT with the finest feature corresponding to 0.34 nm.

In the results of two-dimensional phase retrieval, the reconstructed image area, which shows characteristic features of MWCNT, was limited to the range around 40 nm. It is thought that the finite coherence, namely the angular spread, of the illumination beam restricts the field of view in the reconstructed image.[8,9] The lateral coherence length is defined as $\lambda/2\alpha$ ($\lambda$ is the wavelength of the beam and $\alpha$ is the convergence angle). We performed intensity measurements of the illumination beam without a specimen. The angular spread of the intensity was fitted by a single Gaussian function with $\sigma$=0.068 (±0.007) mrad, which corresponds to the practical convergence angle of the illumination beam. Using this practical convergence angle, for a 20 kV electron beam, the lateral coherence length was estimated to be about 63 nm, which coincides in order of magnitude with the limited area of the reconstructed image. A phase retrieval simulation of a modeled MWCNT with a convergence angle of 0.068 mrad supported this result.[9]

In the case of our system, the probe size on the specimen was estimated to be about 152 nm because diffraction aberration was dominant due to the small convergence angle. The ratio between the probe size and the coherence length was about 2.4, which almost coincides with the condition reported in the previous paper.[7] For a relatively low energy, the coherence length is longer than in the case of higher energy because of the longer wavelength at lower energy for the same convergence angle. We regard a longer coherence length as being an advantage for observing nanocrystals because it let us use larger crystals.

Even in the limited area, the image was not uniformly reconstructed, as shown in Fig. 2(b). There are several possible causes for the unevenness of reconstruction, including background noises in the diffraction pattern. These noises arise from quantum noise, inelastic scattering, and scattering from the specimen grid or apertures in the optics. To reconstruct an image uniformly, it is important to decrease the background noise.

In our experiments, 60 s and longer exposures were done. After these long exposures, the diffraction patterns were not greatly changed, which seems to indicate that no significant radiation damage occurred. This means that our experimental condition with low acceleration voltage of 20 kV might be appropriate for analyses of radiation-sensitive materials (at least for carbon nanotubes).

In conclusion, we executed one- and two-dimensional iterative phase retrieval with diffraction patterns recorded without a postspecimen lens using a 20 kV electron beam. The image reconstructed from the diffraction pattern alone showed a characteristic structure of the MWCNTs with the finest feature corresponded to a carbon wall spacing of 0.34 nm, which coincided with a TEM image of the same specimen.

These results show that our system is suitable for observing radiation-sensitive materials and nanocrystals and should also lead to high-resolution imaging in a low energy range and practical use of lensless imaging.

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