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Atomic structure from large-area, low-dose exposures of materials: A new route to circumvent radiation damage ☆

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ABSTRACT

Beam-induced structural modifications are a major nuisance in the study of materials by high-resolution electron microscopy. Here, we introduce a new approach to circumvent the radiation damage problem by a statistical treatment of large, noisy, low-dose data sets of non-periodic configurations (e.g. defects) in the material. We distribute the dose over a mixture of different defect structures at random positions and with random orientations, and recover representative model images via a maximum likelihood search. We demonstrate reconstructions from simulated images at such low doses that the location of individual entities is not possible. The approach may open a route to study currently inaccessible beam-sensitive configurations.

1. Introduction

The remarkable developments in electron microscopy over the past few years, in particular the correction of lens aberrations [1,2], have improved resolution to such a degree that practically all atomic distances can be resolved [3–11]. At the same time, the reduction of delocalization effects simplifies the analysis of structures on the level of single atoms [12–16]. However, taking advantage of these developments requires that the structures under investigation remain unchanged under extremely high electron doses. For example, discerning individual light atoms typically requires doses well above 10^5 $e^-/Å^2$ [10,16–20].

While radiation damage is a well known bottleneck to the applicability of electron microscopy based methods in biological studies, it has become increasingly relevant also in the study of materials. This is not only because the required signal to noise ratio necessitates higher doses at higher resolution, but also because beam-induced structural changes, which would go unnoticed at a lower resolution, can no longer be tolerated. In the case of low-dimensional materials, such as carbon nanotubes [21], graphene [22], hexagonal boron nitride [23] or mono-layer dichalcogenides [24,25], for which only a single or a few light atoms are present in the projection of a transmission electron microscope (TEM) or scanning-TEM (STEM) image, the problem is at its extreme: the contrast is very low (thus requiring highest doses), the atoms are easily displaced, and at the same time, the position of every single atom (rather than an extended atomic column) is visible and therefore relevant for the analysis.

If knock-on damage dominates the radiation damage, low-voltage microscopy is a viable route to avoid beam-induced changes in the atomic structure [26–32]. Indeed, low-voltage aberration-corrected TEM and STEM have enabled remarkable atomically resolved images of graphene, carbon nanotubes, and other low-dimensional or layered materials [11,15–17,19,20,25,33–49]. Nevertheless, significant beam-driven dynamics are present in all of these studies, especially at defects, edges, or contamination sites. For example, edges of a graphene sheet are still highly dynamic even under 20 kV electron irradiation [30], defects in graphene easily change their shape in 80 kV image sequences [50], and defects are introduced in molybdenum disulfide [25] or hexagonal boron nitride [18,19] under irradiation. It is possible that some configurations completely escape their detection in conventional studies because they decay towards more beam-stable ones within a fraction of the dose needed for high-resolution images. Lower voltages also increase the electron–electron scattering cross section, and hence lead to increased ionization damage. In cases where ionization damage is not suppressed by the high conductivity of a material, it is an order of magnitude larger effect than the atomic displacements [51]. For example, organic molecules typically withstand doses from 10^{-1} to 10^4 $e^-/Å^2$ [52–54,51], which is many orders of magnitude below what is needed for atomic-resolution images of their structure.

An alternative route to circumvent radiation damage is to distribute the dose over many identical copies of an object. This approach is under active development for imaging biological molecules [55–60], where the (very small) tolerable dose limits the available resolution, rather than the instrumental performance of the microscope. Within the single-particle analysis (SPA) [55–60], a large number of images from identical objects are first recorded with very low dose, and then classified into the different orientations (or conformations, if applicable). Finally, averaged

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images with a sufficient signal to noise ratio are calculated. However, this approach only works if the individual exposures contain enough information for the classification. It was estimated that it requires large biological molecules with a molecular weight above 10^5 [61]. Very recently, new methods have been developed to reconstruct electron microscopy and X-ray diffraction data even with individual patterns far below the signal level for direct classification [62–67]. These approaches extract information from correlations in the entire data set, rather than sorting and averaging of individual exposures, relying on the fact that different images of identical objects differ only in a small number of hidden parameters (e.g. their orientation). The study in Ref. [67] showed, among other things, the first case of a reconstruction from simulated TEM data for a biological molecule at a dose where orientation assignment by standard classification was not possible, albeit with only one orientational degree of freedom. However, this idea, i.e., to distribute the dose over many identical configurations within a given sample to minimize the exposure of each object, has not been explored so far for non-periodic configurations in a material.

In this study, we consider localized deviations from a regular lattice in high-resolution TEM or STEM images. We show that it is possible to exploit the multiplicity of identical configurations so that the dose on each object can be reduced by approximately two orders of magnitude, compared to similar quality images of individual entities. The key novelty of our approach is that it works even if the dose in the exposures is too low for locating or classifying individual objects (point defects, functional groups, adsorbed molecules, etc.) in the raw data. The method should be applicable to any case where a finite set of deviations from a regular lattice can be expected to occur repeatedly on a sufficiently large area of the sample. Examples include point defects in a material (shown here for a 2-D material) as well as functional groups or small molecules on the surface of the material.

We begin by quantitatively demonstrating the need for this new approach. Fig. 1 shows simulated HRTEM images of a graphene sheet with a randomly distributed mixture of the three frequently observed types of di-vacancy defects [68], for variable doses. The simulation assumes imaging conditions as used previously [68], and a perfect CCD camera. A dose of ca. 10^4 $e^-/Å^2$ is needed to detect the presence of a vacancy. However, this dose is already almost sufficient to assign the structure (discernible at about 2×10^4 $e^-/Å^2$, and clearly visible at 5×10^4 $e^-/Å^2$). The set of images in Fig. 1 highlights the key reason why previously developed methods for biological structures are of limited use for the case of point defects in a material: they all require that at least the center of mass of the object is known, and in addition each exposure usually must provide some kind of classification (e.g. orientation or conformation type), prior to averaging. Here, however, very high doses are needed already to detect the defect position. This means that any approach that works by classification of individual exposures and subsequent averaging cannot provide a substantial reduction in dose, compared to direct images of individual entities.

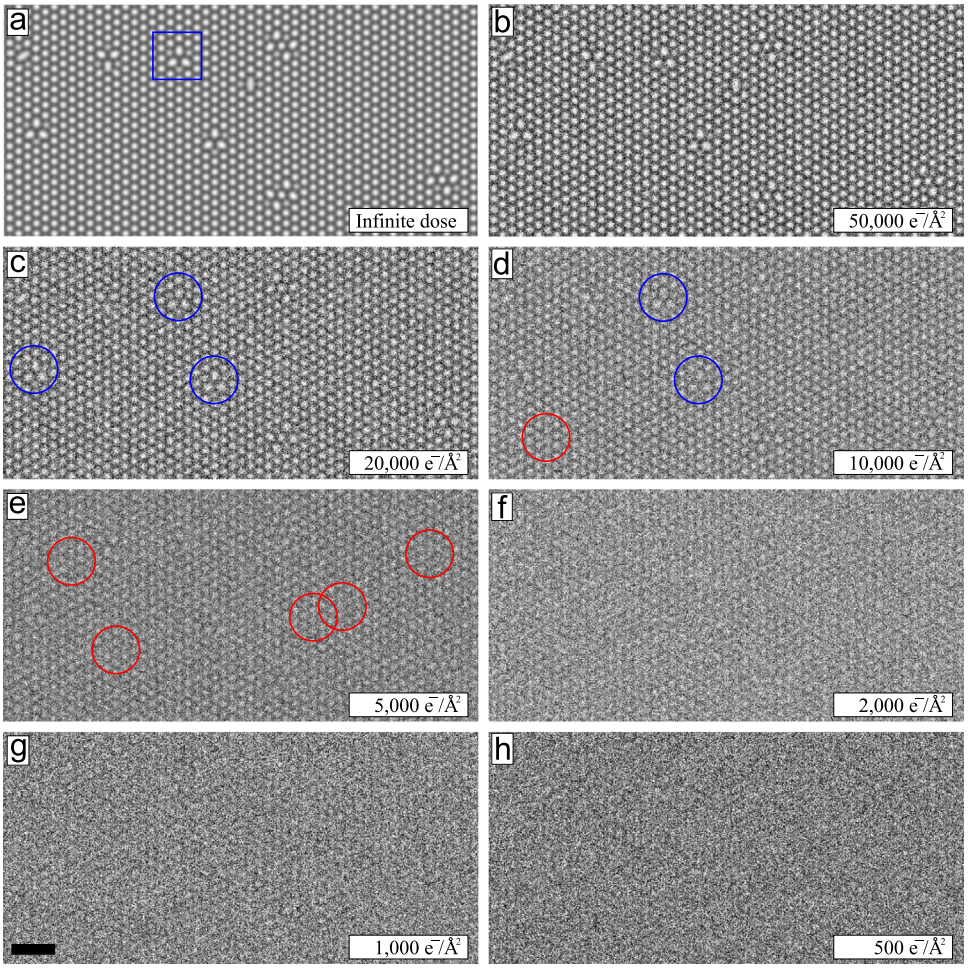

Fig. 1. Simulated HRTEM images of a graphene sheet with a randomly distributed mixture of three di-vacancies, at different doses. (a) Infinite dose simulation, (b–h) finite dose simulation for the same structure, using Poisson noise. From the visual appearance, it becomes difficult to identify the defects at doses below 20,000 $e^-/Å^2$. This can be confirmed by a cross-correlation calculation, using for example the blue box in (a) – the 555777 di-vacancy – as reference: The centers of the circles in (c–e) are placed at the highest three (c, d) and highest five (e) maxima of a cross correlation map that aims to find this structure in the noisy images. Errors occur at 10,000 $e^-/Å^2$, and at 5000 $e^-/Å^2$ it is not possible to locate any of these defects. Scale bar: 1 nm. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

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