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Abstract

Dynamic transmission electron microscopy (DTEM) has the potential to provide insight into nanoparticle catalyst dynamics by obtaining direct images with high spatial and temporal resolution. To date, the limited signal to noise ratios attainable for dispersed nanoparticle samples have made such studies difficult to perform at the highest resolution. These limitations have been overcome by the fabrication of an annular objective lens aperture that permits images to be obtained with a 5 fold increase in the signal to background ratio. This annular dark field imaging mode is shown here to vastly improve the contrast attainable in 15ns pulsed electron images and allows particles as small as 30nm in diameter to be observed.

Dynamic transmission electron microscopy (DTEM) is a recently developed technique that allows *in-situ* TEM images to be obtained with high temporal resolution by using lasers to initiate both a reaction at the sample and produce a pulse of electrons to probe the transient state [1]. The temporal resolution is determined by the duration of the laser pulse that hits the cathode, while the time delay between the two lasers sets the temporal location of the images that are acquired. The current DTEM at Lawrence Livermore National Laboratory (LLNL) incorporates these two laser systems into a base JEOL 2000FX™ 200kV TEM. Here, the first laser pulse, typically with a wavelength of 1064nm, hits the sample initiating the process to be probed. The second laser pulse, at a wavelength of 211nm and approximately 15ns in duration, enters the column where it is reflected by a mirror onto the photocathode. This produces a packet of over 10^9 electrons by photoemission that is also approximately 15ns in duration. This electron pulse is then accelerated down the column onto the sample, forming at image at the detector in the same way as a standard TEM. In this approach to *in-situ* TEM, the temporal resolution comes from the lasers, allowing standard detectors to be used and thus eliminating the limitations caused by the need for an ultrafast shutter.

In this mode of operation, the LLNL DTEM has achieved a spatial resolution of ~8nm with a 15ns pulse from a gold and carbon multilayer test specimen [2, 3]. This test sample exhibits extremely high mass-thickness contrast when compared to typical TEM specimens and as such represents the highest spatial resolution that can be achieved in the microscope. To date, however, low contrast and signal to noise ratios have limited the spatial resolution obtained by the DTEM from less-ideal specimens such as catalyst nanoparticles. In typical bright-field DTEM imaging experiments a large convergence angle is required to achieve sufficient signal to noise ratios for imaging to be successful. The tradeoff for increasing the convergence angle is that the contrast transfer and signal to background ratio are adversely impacted – degrading the overall resolution of the images that are obtained. One mechanism to overcome the degradation in resolution caused by converging the beam is to use annular dark field (ADF) imaging. In ADF imaging, the central disc in the annular objective lens aperture blocks the vast majority of the coherently scattered electrons leaving the incoherent signal as the major contributor to image formation. This produces a dark field image with a vastly higher signal to background ratio allowing even larger beam convergence angles to be used while maintaining high contrast and comparable resolution [4].

ADF-DTEM may also be a significantly better method for imaging on shorter time scales. For a given brightness, there is a non-linear inverse relationship between the pulse length and the attainable resolution, due to columbic interactions [5]. Coulombic repulsion between electrons in the pulse gives rise to two principle effects: pulse broadening due to global space charge and stochastic blurring. The global space charge effect essentially disperses the electron pulse, which can be easily compensated for by the electron optics in the TEM column. The blur is more difficult to deal with as it is caused by random perturbations to the trajectories of individual electrons as the pulse propagates down the column. As the pulse passes through the sample information is encoded in these trajectories so the perturbations effectively blur the resulting image. When using shorter pulse lengths, an ADF aperture enables the user to lower the fluence while compensating for the resulting loss of signal with the increased contrast produced by ADF imaging. The lower fluence reduces the frequency of random coulombic scattering within the pulse, effectively limiting the loss of resolution due to stochastic blur.

ADF apertures were fabricated from 12.5μm thick tantalum foils using a one mask photolithography process. A 1μm layer of aluminum was deposited onto the foils to serve as a hard mask during the etching step. A 7μm layer of SPR220™ positive tone photo resist was spun on the aluminum, exposed using a single mask and immersed in CD-26™ developer for 10 minutes. This developer also etches away the exposed aluminum layer leaving behind exposed tantalum. The tantalum in the exposed areas was subsequently removed using reactive ion etching in sulfur hexafluoride plasma to produce an annular dark field aperture with three support arms. The dry etch was carried out at 80 mtorr, with an SF_6 flow rate of 12 sccm, and a power density of 0.95 W/cm^2. Previous studies on ADF imaging have employed focused ion beams to produce ADF apertures. The aforementioned method of etching refractory metals is ideal in that it is significantly less time consuming, it can be performed in almost any micro-fabrication facility and it can produce a large number of apertures of varying geometries in a single run.

Annular apertures with an outer diameter of 264μm and an inner diameter of 137μm were used in this study. For the 200kV DTEM, this geometry corresponds to an angle of approximately 20mrad at the edge of the central disc and an angle of 40mrad at the edge of the outer aperture hole. This acceptance angle is expected to produce images that are qualitatively similar to those obtained by High Angle Annular Dark Field Scanning TEM (HAADF-STEM) so that the contrast is strongly correlated to the atomic number of the material[6, 7, 8]. A major difference between the two techniques is that more coherent scattering contributes to the image contrast in ADF-TEM since not all Bragg reflections are blocked by the aperture. Figure 1 shows overlaid diffraction patterns from gold nanoparticles on a holey carbon film with and without the ADF aperture inserted. The aperture blocks the Bragg reflections out to approximately 10mrad allowing only extremely weak reflections to contribute to the image formation.

This ADF geometry is ideal for imaging the dynamics of catalyst particles on low atomic number substrates. The catalyst sample used in this study consisted of gold nanoparticles ranging in size from 1 – 100nm dispersed on a holey carbon film. Figure 2 shows a conventional TEM image of the sample area as well as single shot pulsed images at 15ns time resolution in both bright field and dark field. In the time resolved bright field images most particles below 50 nm are not resolved due to limited signal and low contrast. In the time resolved dark field equivalent almost every 50nm particle and many 30nm particles are clearly visible. The stark difference between these two images clearly demonstrates the efficacy of annular dark field imaging when dealing with samples with feature sizes near the resolution limit of DTEM. The line scans are integrated over a 5 pixel wide area and are taken across the same feature in each image. From this data the signal to background ratio was determined to be 0.362 for pulsed bright field and 1.16 for pulsed ADF. The line scans demonstrate that while effects such as stochastic blur still have an impact on resolution and the overall noise level, the more than 3 fold increase in signal to background ratio obtained by ADF imaging makes it far easier to discern significant features when compared to conventional bright field pulsed imaging. The ability to obtain vastly improved contrast for smaller particles widens the range of catalyst systems that can be usefully studied using DTEM.

Video-rate in situ studies of catalyst materials have led to important insights into processes such as nanowire and nanotube growth. The improved time resolution offered by dynamic transmission electron microscopy (DTEM) stands poised to offer far greater insight into the mechanisms behind many catalytic processes[9, 10]. The contrast improvements offered by ADF imaging will enable DTEM studies on catalyst sintering and Ostwald ripening which are critical limiting factors in the growth of single walled carbon nanotube forests and nanowires of various compositions [11, 12]. The DTEM drive laser can easily produce temperatures required for catalytic growth of such materials. Under these conditions, with the aid of ADF imaging, it will be possible to observe the diffusion of catalyst material and discern mechanistic details about the growth of nanostructures.

In conclusion, we have demonstrated that ADF DTEM imaging is a viable method for obtaining time resolved images of catalyst nanoparticles. This method significantly increases the contrast and signal to background ratio of DTEM images. Moreover it is capable of resolving smaller particles than conventional bright field DTEM. This technique enables imaging studies on the dynamic behavior of catalysts at high temperatures with nanosecond time resolution. This will open a window into the particle-substrate and particle-particle interactions that lead to effects such as nanoparticle sintering, Ostwald ripening, catalyst poisoning, and nanowire growth.

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Figures:

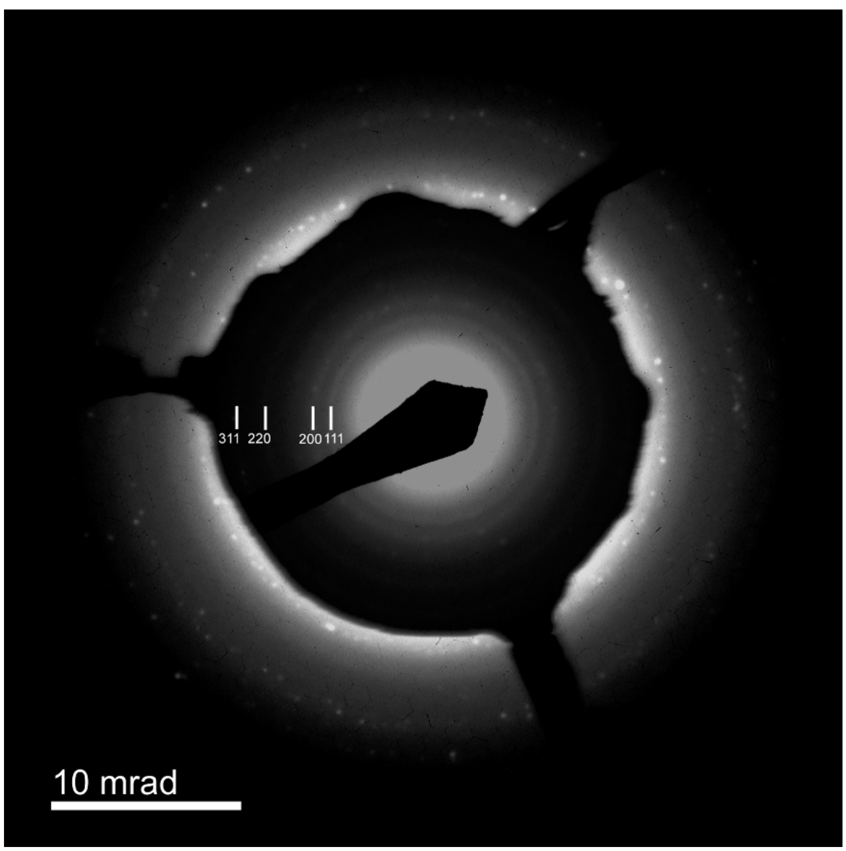

Figure 1. Overlaid selected area diffraction patterns from Au nanoparticles with and without the ADF aperture inserted. The exposure with the ADF aperture inserted was 10 times longer than the exposure without the aperture.

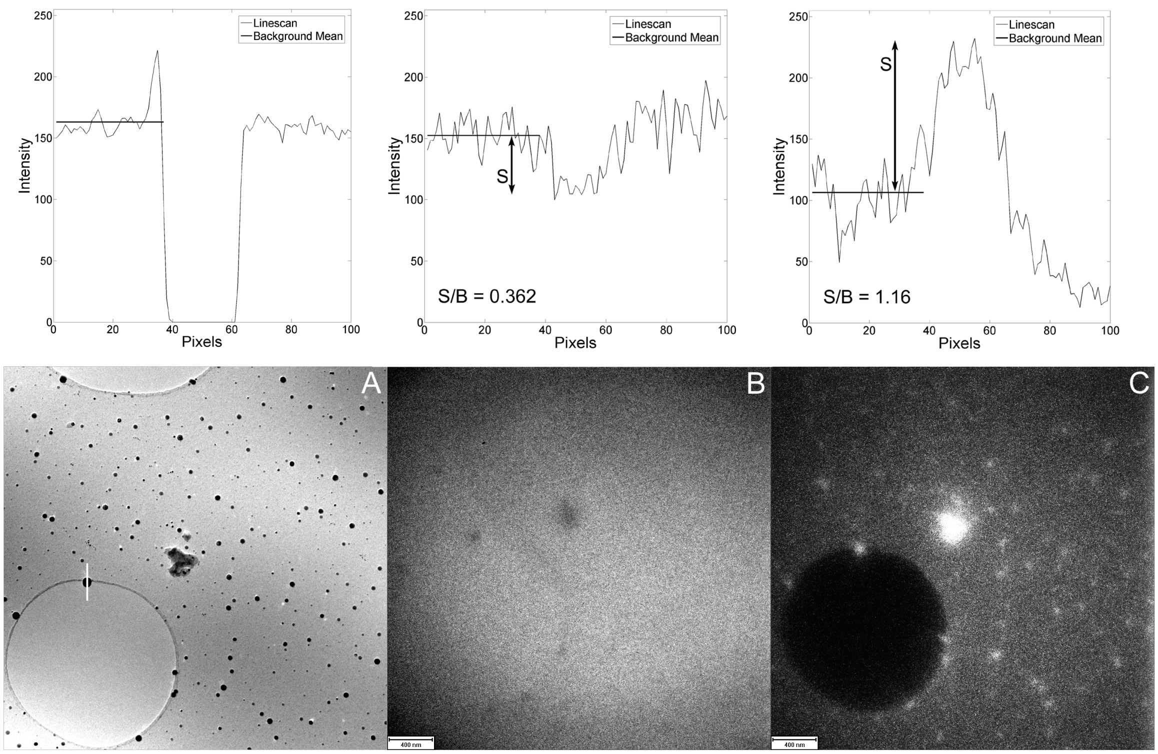

Figure 2. A: Conventional TEM image, the white line shows where the line scans were taken B: 15ns pulsed bright field image C: 15ns pulsed ADF image. The scale bar is 400nm. The line scans show the improved signal to background obtained by using an ADF aperture for pulsed imaging.