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Optimizing STEM Imaging Conditions Towards Reliable Representation of Single Atom Catalysts

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Single-atom catalysts (SACs) are emergent catalysts whose active sites are present as isolated metal atoms [1]. Probing atom dispersion and their interactions with each other and with support, especially the formation of dimers, trimers, or even clusters, is the key to understanding the catalytic properties of SACs, such as activity and stability. Scanning transmission electron microscopy (STEM) high-angle annular dark-field (HAADF) imaging has primarily been used to image single atom distributions. However, it is frequently reported that single atoms on a support can be activated by an incident beam to diffuse along the surface [2, 3, 4, 5], opening the question of how reliable the acquired positions might be. In this work, we aim to investigate the mechanism of beam irradiation in single atom heterogeneous catalysts and identify the optimum experimental conditions. In particular, we evaluate how electron dose, dose rate, voltage and cryogenic temperature impact beam irradiation on SACs.

In this study, we use Pt on graphitic C_3N_4 (Pt/g-C_3N_4) as a model SAC system. This system shows great potential for photo- and electro- catalysis [6, 7], and is representative of a large family of heterogenous catalysts containing precious metal single atoms on semiconducting amorphous supports. The polymeric and semiconducting nature of C_3N_4 makes it potentially susceptible to multiple irradiation processes, including knock-on, radiolysis, and electrostatic charging. These properties make Pt/g-C_3N_4 a good platform to investigate beam-specimen interaction for SACs. To analyze atomic motion under various experimental conditions, we acquired a series of HAADF movies with frame times of about 2 seconds. By varying accelerating voltage, beam current, and specimen temperature, direct comparisons are made to determine which factors are relevant to Pt/g-C_3N_4.

Figure 1. shows the procedure used for post processing. Images were first processed to enhance atoms contrast by applying a smooth filter and a bandpass filter. To directly compare between different imaging conditions, three consecutive frames within each movie were taken out and color-coded to form color composite image. As a result, moving atoms will show as colored peaks while stable atoms will present as bright white spots in composite images. Figure 2. shows a subset of composite images with different imaging conditions. In Figure 2.a and d., atoms are more in white color while for b. and c. atoms are shown as colored dots, indicating strong atomic motion. More careful comparison between Figure 2.a and d. shows a further reduction of atomic motion when reducing the beam current. Such observations can be largely explained by knock-on displacement as the main mechanism for atomic motions.

To summarize, we have qualitatively explored the influence of accelerating voltage, beam current and specimen temperature on atomic motion in Pt/g-C3N4. We found that reducing accelerating voltage and beam current can effectively help mitigate the atomic motion, while operating at cryogenic temperature does not show an obvious benefit in this case. These observations can be explained as the result of knock-on displacement being the dominant factor for atomic motion. Although the mechanism of irradiation driven motion can differ between systems, optimization of imaging condition should be considered as an important preliminary for detailed characterization to reduce spurious beam effects [8].

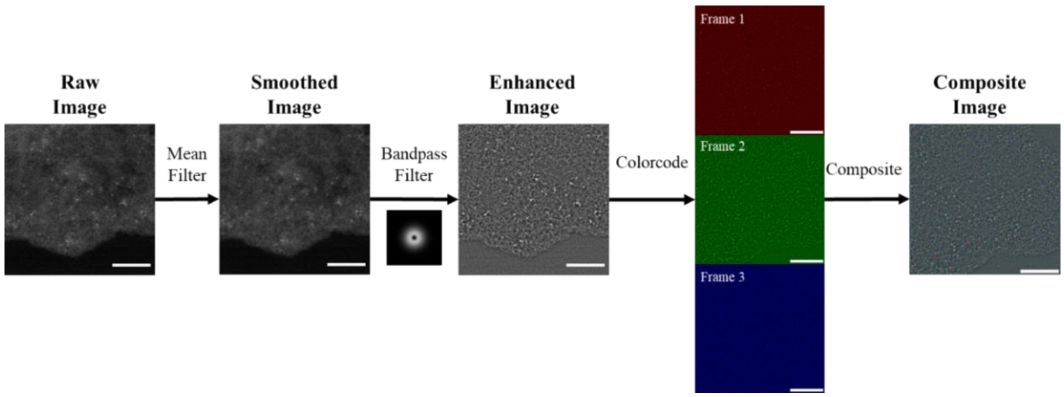

Figure 1. Procedure for atom enhancement and color composite. After filtering, three consecutive frames are assigned as one channel for RGB composite. The overall color shown in composite image is due to mean intensity difference of different frames after filtering. Scale bar is 5 nm.

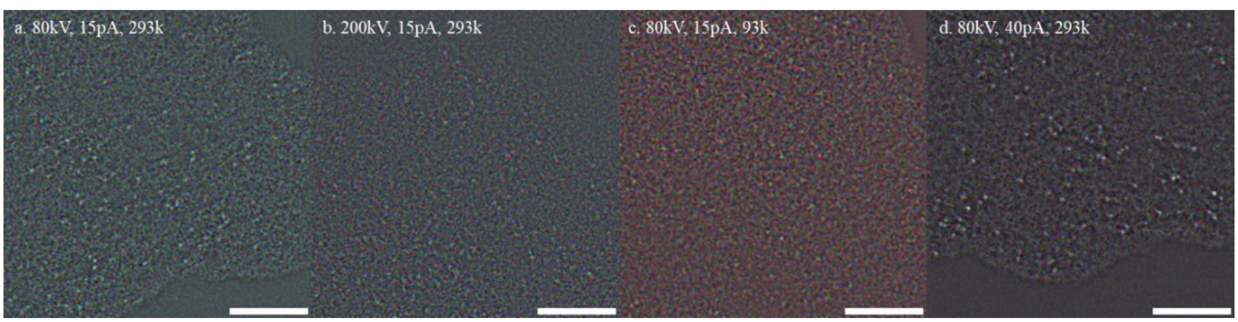

Figure 2. Comparison of atomic motion with different imagining conditions. Imaging conditions are labeled in each image. Stable atoms present as bright white dots, other atoms show as colored peaks. Scale bar is 5 nm.

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