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Dear Editor,

Please find our uploaded manuscript “Quantum theory of electron excitation and sputtering by transmission electron spectroscopy” that we are hereby submitting for consideration as an article in *ACS Nano*.

Electron beam irradiation by transmission electron microscopy (TEM) is an effective tool for defect engineering in 2-dimensional (2D) materials, potentially with atomic-scale precision. This degree of spatial control can provide powerful solutions to many of today’s most pressing challenges in nanotechnology, including quantum device fabrication, hydrogen evolution catalysis, and electronic device miniaturization.

However, despite the broad application of TEM-driven defect engineering in materials science, current theoretical models fail to quantitively describe defect formation rates, as the non-equilibrium physics taking place during irradiation remains poorly understood. Specifically, existing models drastically underestimate sputtering rates in insulators, in which beam-induced electronic excitations may weaken the bonding between the irradiated atoms. To address this anomalous behavior, this work develops the first quantum electrodynamics (QED)-based method to accurately describe electron beam-induced sputtering cross sections in 2D crystals by explicitly calculating the probabilities of beam-induced electronic excitations and their effects on sputtering kinetics. The consideration of excitations yields cross sections that quantitatively match experiment and correctly predict appreciable sputtering rates at beam energies previously predicted to leave the crystal intact. This new quantitative theory can pave the way for the use of TEM for top-down atomic-scale defect engineering of 2D insulators.

We feel that this work meets the acceptance criteria of *ACS Nano*, as it significantly advances the state of the art in modelling the nanoscale response of materials to TEM irradiation. As nanoscale sculpting and degradation by TEM have been investigated in several impactful *ACS Nano* articles (see for example 10.1021/acsnano.6b08324, 10.1021/acsnano.6b01419, and 10.1021/nn4044035), we believe this work will appeal to the *ACS Nano* readership. The QED-based prediction of excitation rates could also push efforts to simulate both TEM images and electron energy loss spectra towards a more analytical, quantum field theory-based direction. Lastly, we believe this new predictive power can help arm materials scientists and engineers with precise nanoscale control of any 2D material.

The Supporting information includes detailed derivations of several equations in the main text. It also contains plots describing the convergence of various parameters. The Mathematica notebook generates an expression used in the derivation.

Thank you for your consideration.

On behalf of all the authors,

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