Visualizing the dynamics of low-energy electron-matter interactions using in-situ fluorescence microscopy

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Understanding and directing the reaction pathways of molecules with energetic electrons is important for a wide variety of technological applications such as electron- and XUV-lithography, electron-beam induced deposition, and electron microscopy. In most cases, reactions with low-energy secondary electrons (energies of <50eV) generated in the environment of the molecule, have cross sections dominating over contributions from higher energy electrons. For these low energy electrons, there can be many different degradation and/or dissociation pathways involved on a molecular level. [1] Disentangling the different contributions can be challenging, especially for complex but relevant samples such as polymers, organic compounds, and biological tissues. Typically, one evaluates in some experimental way the end products obtained after reaction, leaving transient dynamics obscured. Here, we present a novel approach to study low-energy electron induced molecular degradation by using in-situ fluorescence microscopy during electron irradiation of organic fluorescent molecules to report on the reaction kinetics.

We use a SECOM fluorescence light microscope integrated in a FEI Verios 460 scanning electron microscope (Fig 1a). [2][3] Electron beam landing energies are controlled to single eVs by applying a negative stage bias with an accuracy of 0.3 eV (Fig. 1b). For preliminary experiments, we used a sample of fluorescent perylene diimide molecules spin-coated on a glass/ITO substrate that was coated with a 10nm thick Al_2O_3 layer to prevent quenching by the ITO. [4]

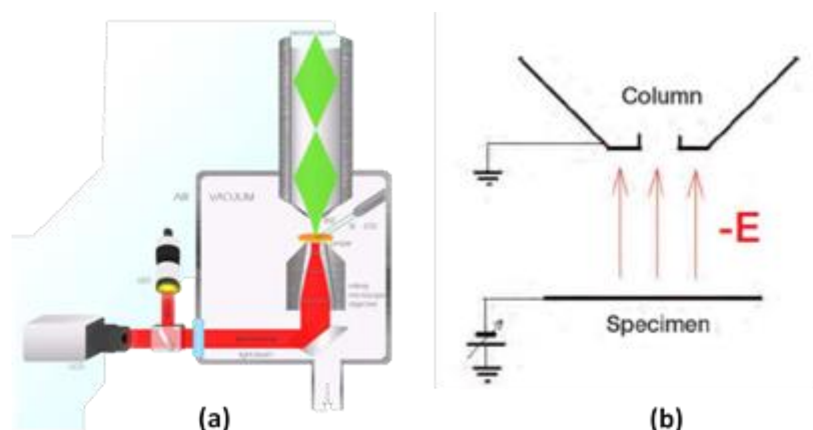

Figure 1 (a) Schematic for integrated microscopy where fluorescence microscopy (optical path indicated in red) can be performed simultaneously with scanning electron microscopy (optical path indicated in green). (b) The electron landing energy is controlled with a negative stage bias decelerates electrons leaving the column.

We monitor the luminescence intensity of the fluorescent dye using continuous light illumination while exposing the perylene dye to fixed low electron doses for landing energies ranging from 1 to 50 eV. Our first results show an electron-energy dependent decrease in fluorescence after irradiation, followed by a fractional recovery of the fluorescence intensity (see Fig. 2). We will discuss these results in terms of electron interaction cross-sections and models for the observed recovery of fluorescence intensity. We will also discuss the potential role of photo-excitation during the recovery process.

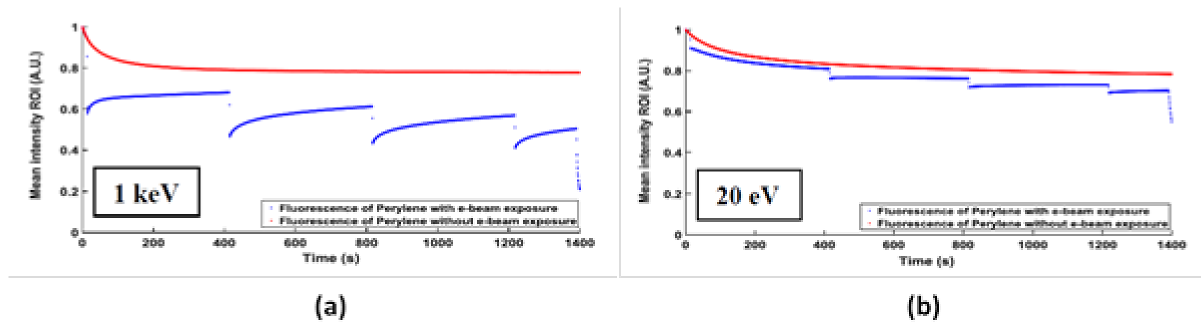

Figure 2 (a) Relative fluorescence intensity bleaching curve with (blue curve) and without (red curve) e-beam irradiation under continuous illumination. Strong drops in intensity correspond to electron beam exposure with a dose of D= $1.35 \cdot 10^{-3} C/m^{-2}$ **and landing energy of (a) 1 keV (b) 20 keV. The final drop corresponds to a high-dose electron irradiation.**

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