

Electronic Supporting Information – Enhancing the Feasibility of Pd/C-catalyzed Formic Acid Decomposition for Hydrogen Generation – Catalyst Pretreatment, Deactivation, and Regeneration

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NMR measurements

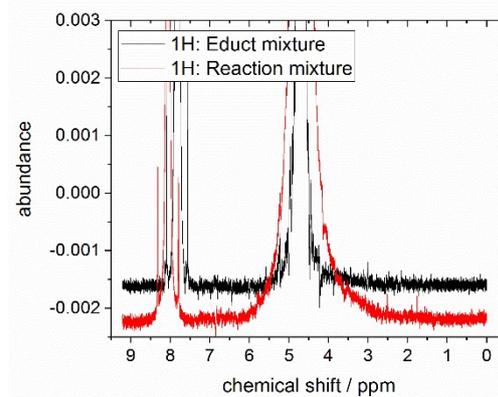
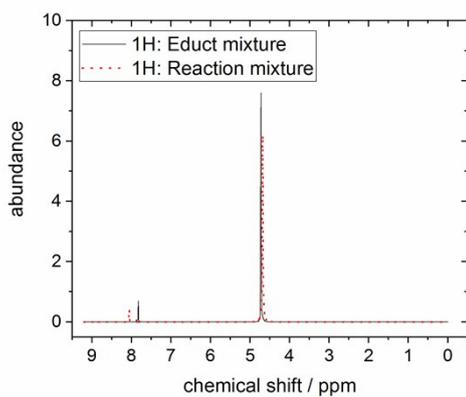


Fig. S1: ^1H -NMR.

The chemical shift at 8 ppm belongs to the protons of water. The chemical shifts around 4.6 ppm belong to the proton of the C-H-group FA or formate that is shifted because of different concentrations.

Catalyst loading

Table S1: Comparison of the catalyst metal loadings of fresh and deactivated Pd/C before and after FAD.

Material	Metal loading / wt%
Fresh Pd/C	4.9
Pd/C after FAD	4.5
Pd/C after regeneration and recycling	4.6

Investigation of the BET-surface of the catalysts

Table S2: Comparison of the catalyst BET-surface of fresh and deactivated Pd/C before and after FAD.

Material	BET-surface / m ² g ⁻¹
Fresh Pd/C	662
Pd/C after FAD	630

Experimental section on TEM

The TEM measurements were performed with a Philips CM30 transmission electron microscope at the Center for Nanoanalysis and Electron Microscopy (CENEM). We used a voltage of 150 - 300 kV and the particle size distribution was evaluated with the ImageJ software package.¹ To account for deviations, we evaluated 501 particles of the fresh Pd/C catalyst and 1851 particles of the used Pd/C catalyst.

Characterization of the catalysts by TEM before FAD

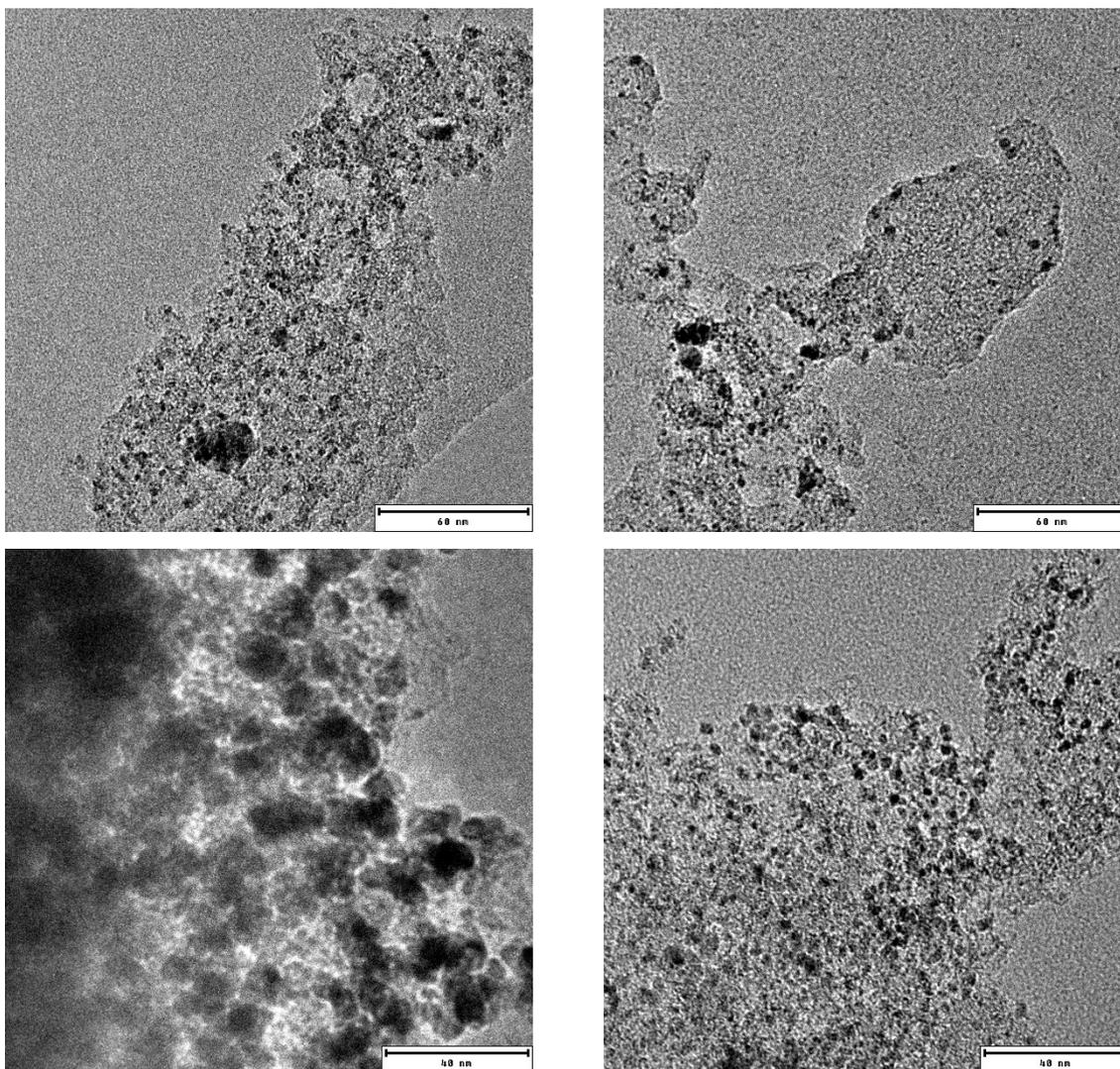


Fig. S2: TEM of fresh Pd/C before FAD.

Characterization of the catalysts by TEM after FAD

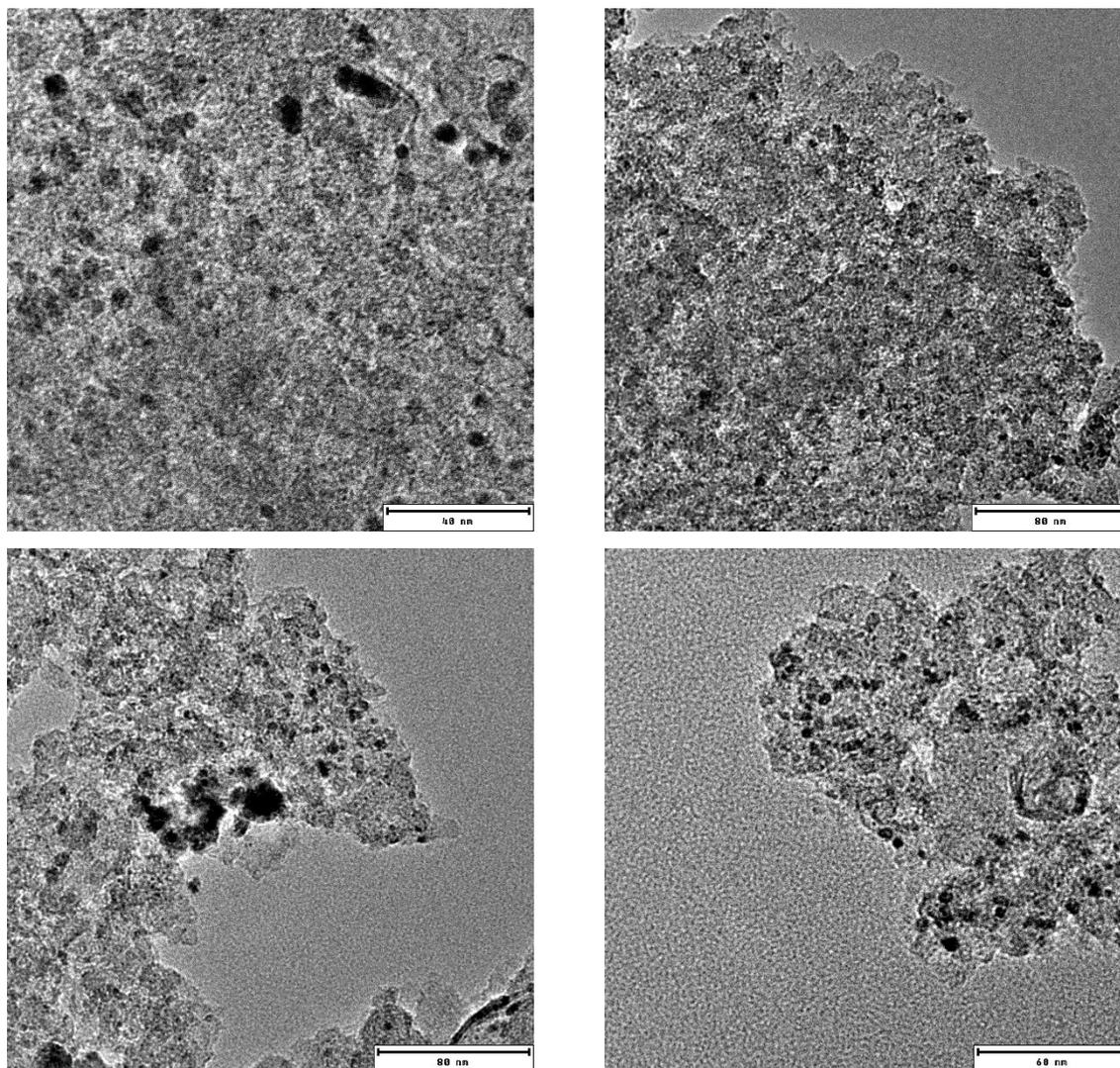


Fig. S3: TEM of deactivated Pd/C after FAD.

Size distribution of the Pd nanoparticles

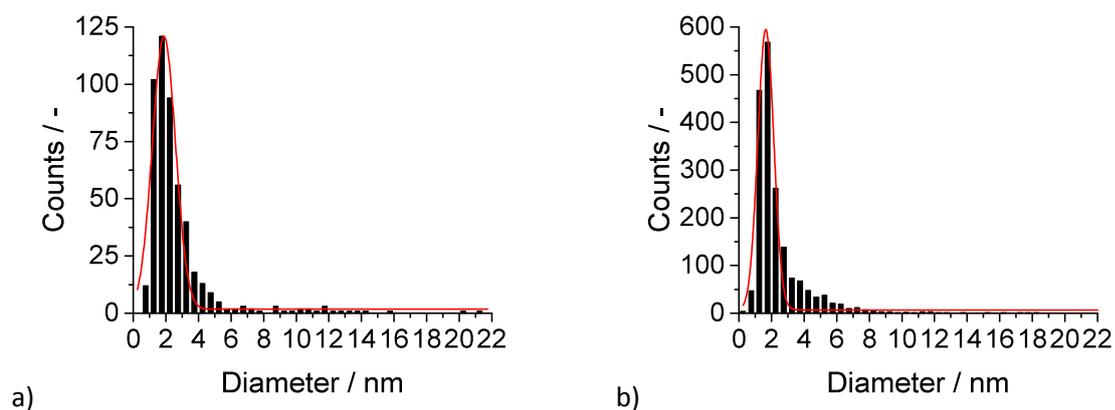


Fig. S4: Palladium particle size distribution from TEM measurements of a) fresh Pd/C before FAD and b) deactivated Pd/C after FAD.

In Figure S4, the particle size distribution as obtained by TEM is shown for a fresh (Figure S4a) and used Pd/C catalyst (Figure S4b). For the fresh Pd/C sample, the average size distribution was 1.9 ± 0.7 nm. The deactivated catalyst showed an average size distribution of 1.7 ± 0.5 nm. As the size of the Pd clusters remains constant, agglomeration is excluded to cause the deactivation of the Pd/C catalyst during FAD.

DRIFTS measurements on pristine Al_2O_3

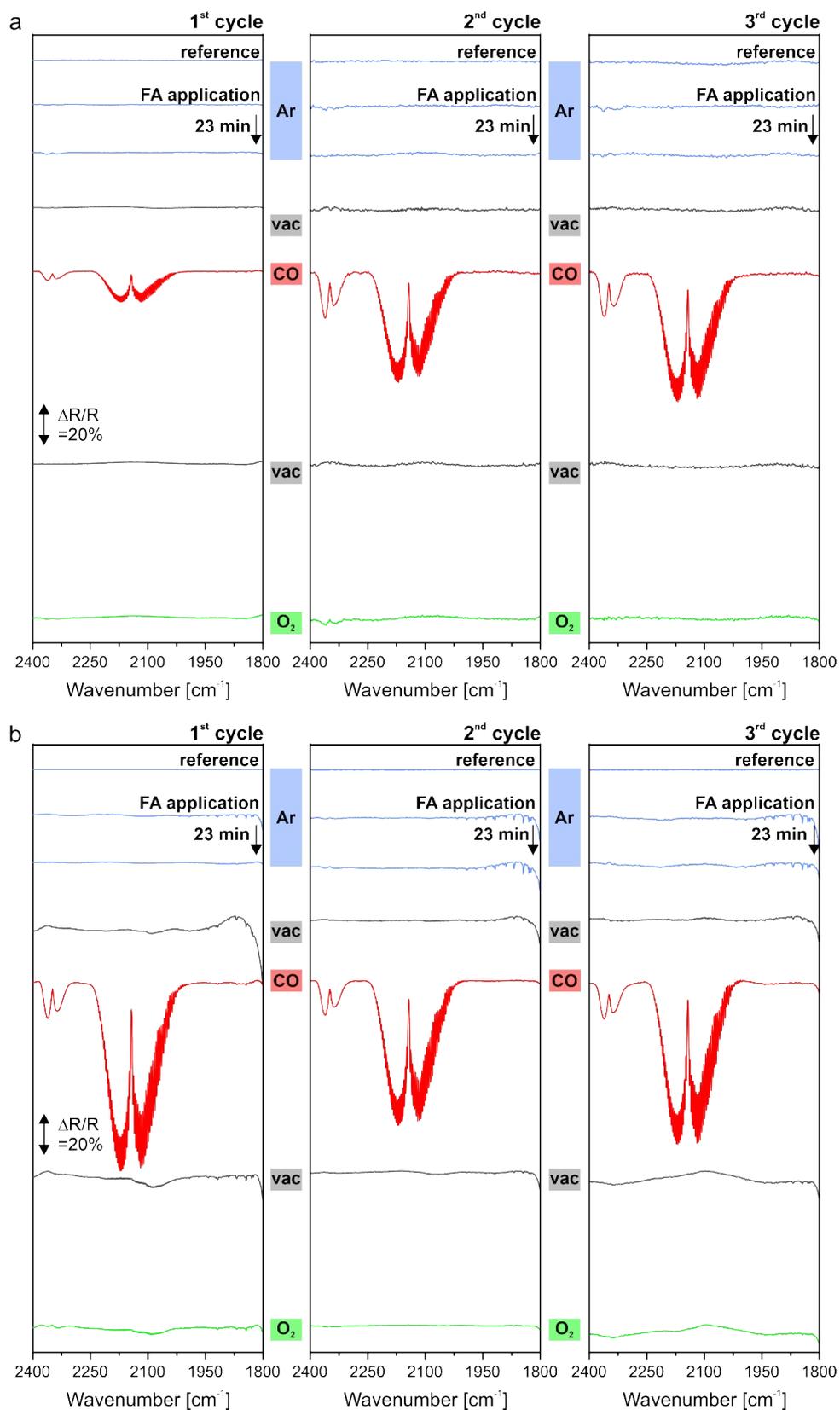


Fig. S5 Offset DRIFT spectra recorded during three cycles of Ar, FA, CO, and O₂ dosing with intermediate evacuation on a) O₂-pretreated Al₂O₃ and b) H₂-pretreated Al₂O₃; m_{cat} = 0.1 g; 20 vol% HCOOH; T = 30 °C; p(Ar) = p(CO) = p(O₂) = 1 bar; p(vac) = 1 mbar.

Fingerprint region during FAD

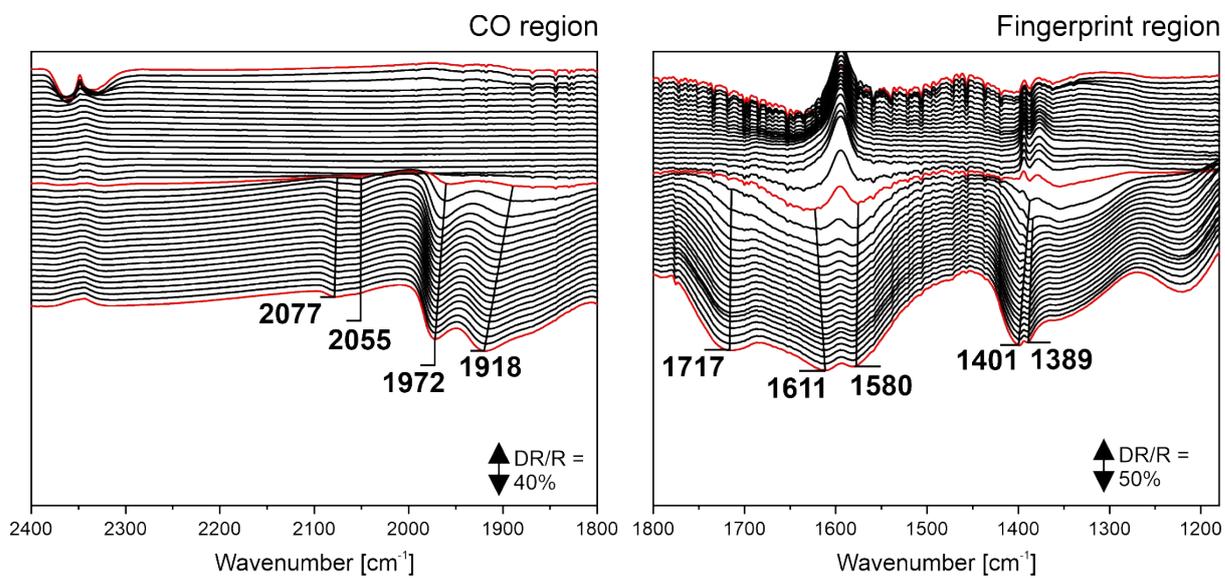


Fig. S6: Time resolved spectra during the evacuation interval in the CO and the fingerprint region.

All cycles including intermediate H₂ treatment

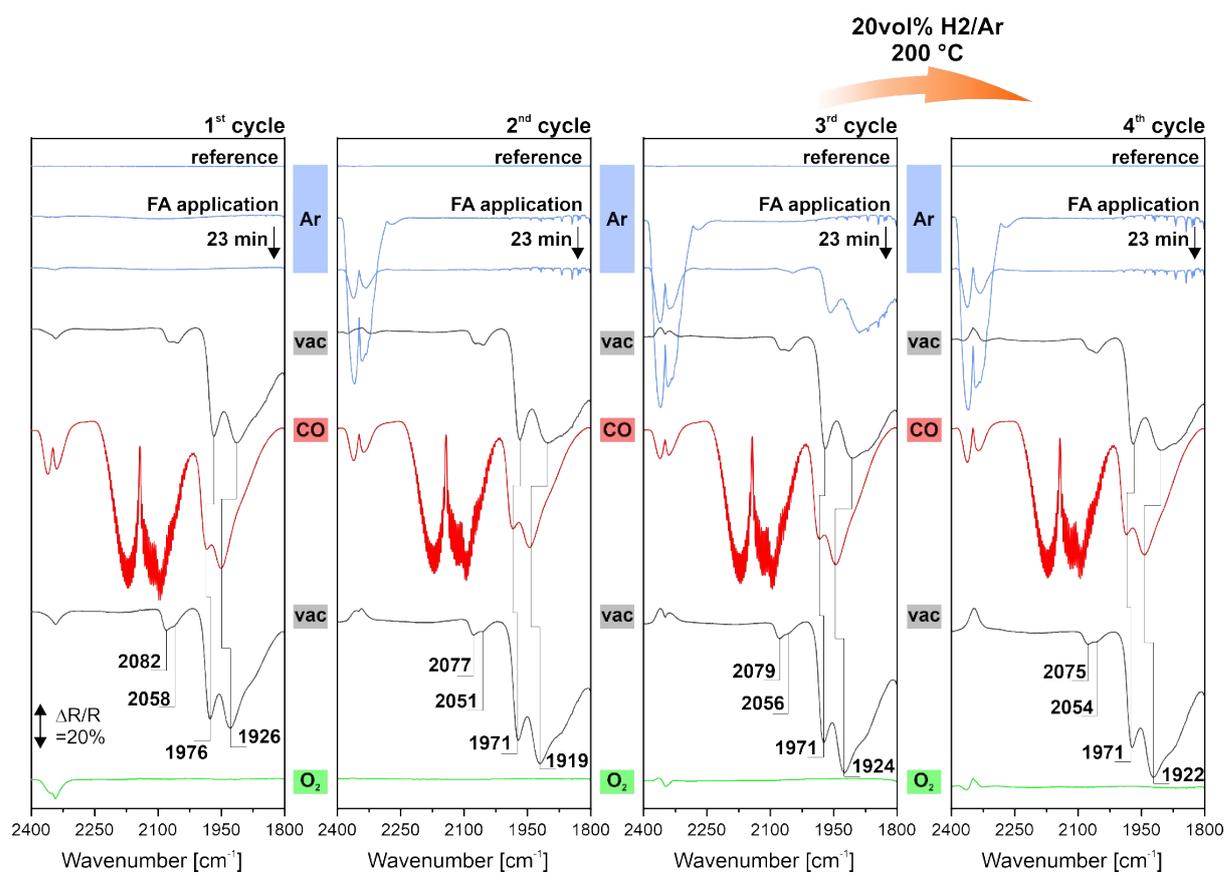


Fig. S7: All dosing cycles of (O₂+H₂)-Pd/Al₂O₃ sample; $m_{\text{cat}} \approx 0.1 \text{ g}$; 20vol% HCOOH; $T = 30 \text{ }^\circ\text{C}$; $p(\text{Ar}) = p(\text{CO}) = p(\text{O}_2) = 1 \text{ bar}$; $p(\text{vac}) \approx 1 \text{ mbar}$.

References

1. C. T. Rueden, J. Schindelin, M. C. Hiner, B. E. DeZonia, A. E. Walter, E. T. Arena and K. W. Eliceiri, *BMC Bioinf.*, 2017, **18**, 1-26.