Supporting Information

Simple and effective in-situ sample illumination for Electron Paramagnetic Resonance

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S1 Optical set-ups



Figure S1. Coupling of EPR tube with the LED light source M455F3 (Thorlabs) for effective *in situ* sample illumination: the top of the tube is shown with the position of the collar that locates the LED source at the top of the tube.



Figure S2. Photos of the LED/tube assembly, with the sample area wrapped with two layers of PTFE tape: LED light is off (left); LED light is on, the image is overexposed (centre); image exposure is adjusted to show the predominant illumination of the sample area (right).



Figure S3. Photos of the LED positioned at the exposed end of the tube for longitudinal illumination into the tube (left), and at the side for perpendicular illumination through the optical window (right). Note that for the longitudinal illumination arrangement, the distance between the LED and the sample is actually larger than for the perpendicular illumination, however, the light intensity delivered into the sample is much higher.

<u>S2 EPR data</u>

Table S1. Parameters used for time dependent continuous wave EPR experiments presentedin Figure 2

Parameter	Value
Microwave attenuation	20 dB
Microwave Power	2.2 mW
Modulation Amplitude	10 G
Time constant	81.92 ms
Conversion time	5.01 ms
Sweep time	20 s
Sweep width	100 G
Centre field	3512.9 G
Receiver gain	30 dB
Microwave Frequency	9.83 GHz

Table S2. Parameters used for the end point continuous wave EPR experiment presented in figure 1.

Parameter	Value
Microwave attenuation	20 dB
Microwave Power	2.2 mW
Modulation Amplitude	0.5 G
Time constant	81.92 ms
Conversion time	5.01 ms
Sweep time	20 s
Sweep width	100 G
Centre field	3521.05 G
Receiver gain	30 dB
Microwave Frequency	9.83 GHz



Figure S4. Waterfall stacked plots for complete dataset of time dependent continuous wave EPR traces measured for perpendicular illumination through the optical window.



Figure S5. Waterfall stacked plots for complete dataset of time dependent continuous wave EPR traces measured for vertical illumination with an etched tube.



Figure S6. Waterfall stacked plots for complete dataset of time dependent continuous wave EPR traces measured for vertical illumination with a PTFE wrapped tube.



Figure S7. Plots to show linear regression fits (red line) of experimental data (black points) used to calculate initial rates of radical generation presented in Table 1 in the main text.