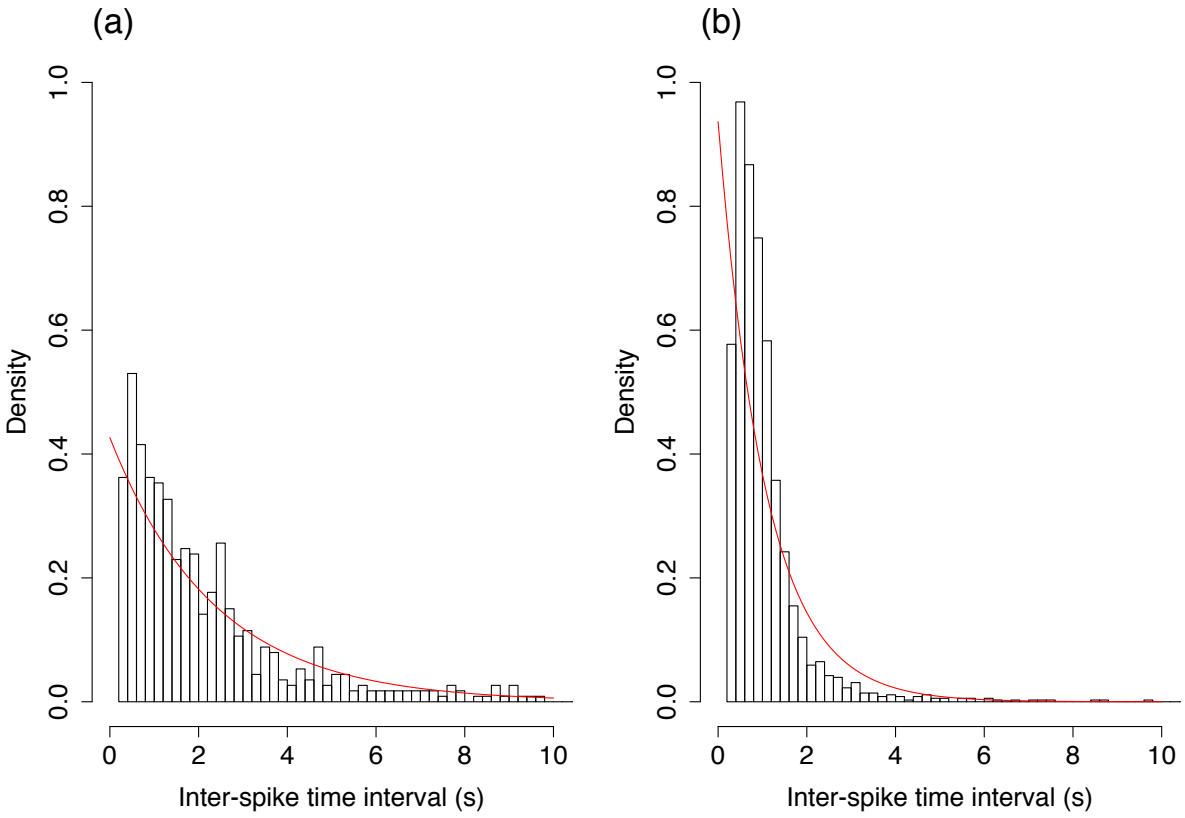
Electronic Supplementary Information (ESI)

ESI- Figure 1 | *Interpeak interval histogram fitted to an exponential distribution*. Inter-spike interval histograms are extracted by counting the number of inter-spike intervals falling in various time bins. Assuming collision events are independent from each other and follow a homogeneous Poisson distribution, the interspike interval is given by an exponential decay function e^{-rt}, with rate r= 0.42±0.01 s^{-1} and 0.93±0.02 s^{-1} for 10 pM catalase in the absence **(a)** and presence of H_2O_2 **(b).** These rates correspond to a mean inter-spike time interval of 2.4s and 1.1s respectively.



ESI-2| *Fluorescence Correlation Spectroscopy (FCS) setup and data analysis*

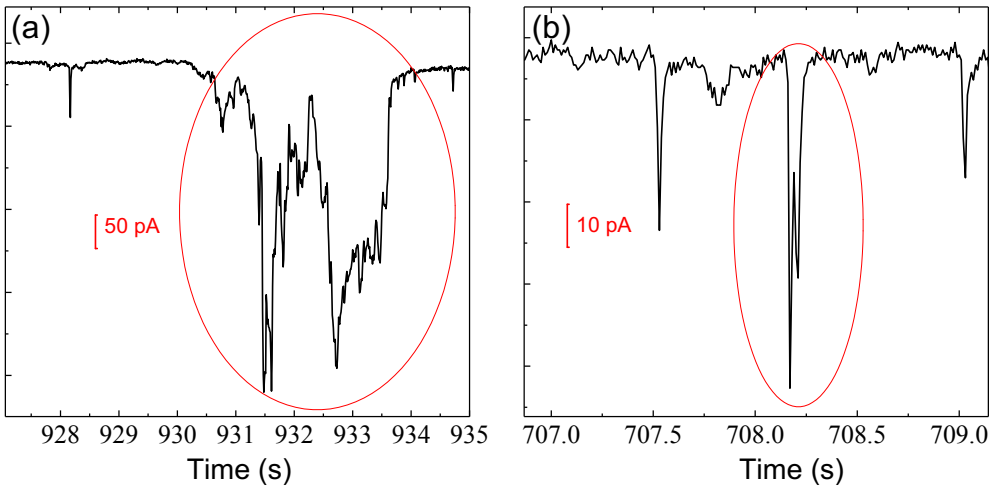
A custom-built confocal setup was used equipped with an incident CW laser 532 nm Nd:YAG laser (Samba, Cobolt) coupled with a 60x, 1.35 NA, UPlanSApo oil immersion objective (Olympus) and a dichroic mirror (630DRLP, Omega) to spectrally separate excitation and emission beams. An avalanche photodiode (SPCM-AQR14, Perkin Elmer) collected single-photons and the produced signal was processed using a multiple-tau digital correlator (Flex, Correlator) to generate autocorrelation functions $g_2(t)$ shown in Figure 5a. Curves were then fitted to single-species diffusion model below using a least-squares regression algorithm:

$$g_2(\tau) = \frac{1}{< N >}\left(1 + \frac{\tau}{\tau_D}\right)^{-1} \cdot \left(1 + \frac{\tau}{SP^2\tau_D}\right)^{-1/2}$$

<N> is the average number of fluorophores in the observation volume, SP is the structure factor (ratio between height to width of the confocal ellipsoid volume) callibrated with a reference fluorophore (Rhodamine 6G). $\tau_D = r^2/4D$ is the characteristic diffusion time, out of which the diffusion constants and their ratios are extracted (Figure 5b).

ESI-3| *Representative spikes originating from multi-particle collisions.*

Spikes with longer residence time a) and higher peak area b) corresponding to multi-particle collisions at the electrode. These type of spikes constitute less than 1% of the total observations.



ESI-4| *Representative spikes at applied potentials of -0.3 V and -0.4 V.*

Representative spikes from i-t curves at BDD-ume in solution containing 0.1 M PBS and 10 pM catalase at applied potentials of -0.3V in a) and -0.4 V b), respectively.