Supporting Information for "Chemotaxis of Catalytic Silica-Manganese Oxide 'Matchstick' Particles"

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Experimental Methods

Materials

PVP-K30 (Average M_w = 40,000), 1-pentanol (99%), sodium citrate dihydrate (99%), manganese (II) sulfate (>99%), tetraethylorthosilicate -TEOS (99%), hydrogen peroxide (30 vol.%) and paraffin wax (m.p. 73-80°C) were obtained from Sigma-Aldrich, and used as received. Ethanol was of AR grade (99.7-100%) and concentrated ammonia (18.10M) was of no older than 2 months (Important in the rod synthesis)[1] - both from Fisher Scientific. Briwax and Vaseline were obtained from local hardware shops.

Synthesis and purification of SiO_2-Mn_xO_y composite matchstick particles

A modified recipe to that outlined by Van Blaaderen was adopted,[1] whereby the modification involved doping of the aqueous phase with manganese sulfate. Stock solutions of PVP-K30 (100g L^{-1}) in 1-pentanol, sodium citrate (0.18M aq.), and manganese sulfate (0.1M, aq.) were made. Note that the PVP-K30 was dissolved by 2 hours of sonication, followed by stirring overnight. Then in a 50mL Eppendorf centrifuge tube the following were added: Pentanol-PVP (30mL), ethanol (3mL), sodium citrate solution (0.2mL, 0.18M), and metal sulfate solution (0.84mL, 0.1M). The mixture was shaken well by hand for 30 seconds to generate a slightly opaque emulsion of water in pentanol. At this point ammonia was added (0.5mL, 18.10M), and the emulsion turned orange/brown in colour. The sample was left for one minute before the addition of TEOS (0.3mL). Particles were cleaned by three rounds of centrifugation for 15 minutes at 4200g into ethanol/water (50/50 vol. %). As the direct synthesis results in a fairly polydisperse size range of metal oxide loaded silica rods, a selective centrifugation procedure was applied to the solution to achieve a narrower polydispersity for analysis. Three rounds of centrifugation were performed for 15 minutes at 120g, redispersing in water (keeping solids), followed by a further three rounds of centrifugation for 15 minutes at 30g (keeping supernatant).

Characterization of the SiO_2-Mn_xO_y rods

SEM samples were prepared by diluting the matchstick solutions to around 0.01 wt% in DIW, and allowing them to dry on silicon wafers supported by an aluminium stub. Sputtering was then performed with a gold target at 25kV for 40 seconds to give a layer thickness of 5nm. SEM imaging was performed on a Zeiss Supra 55VP at 10kV. For TEM image analysis and EDAX, samples were mounted on a lacey carbon copper grid, and imaged with a JEOL 2000FX TEM equipped with an EDAX detector. XRD measurements were performed on a Bruker D5000 from 25-850°C, and between scattering angles of 10-80°. For higher resolution patterns the analysis was collected over 24 hours following calcination of the sample at 850°c in air.

Studying the ballistic propulsion of the particles

Particle tracking measurements were performed with a Nanosight LM10 running NTA 2.3 software at 20x magnification and with a calibration of 170nm/pixel (1 $pixel^2$ = 0.029μm^2). The particle concentration of the rods was approximately 5 x 10^8/mL. To investigate the effect of the concentration of H_2O_2 on ballistic propulsion, suitable concentrations of H_2O_2 solutions were made up immediately prior to analysis, and kept wrapped in tin foil. Then, H_2O_2 solution (0.3ml), and particle solution (0.5mL) were mixed together in a vial before injection into the sample cell. Video clips were typically taken for either 90 or 160 seconds at 30 frames s^{-1}, and filters were put in place to only track particles present in at least 121 frames, to ensure a large number of data points were included in the plots of Δt ranging from 1/30s to 2s.

Following analysis of the video clips, the x and y coordinates for each particle were output as a function of frame number, and a custom java script (can be found at www.bonlab.info) was run on each separate particle file to calculate the mean-squared displacement at each time interval = 1/(frame rate) (**Equation 1**).

$$MSD = \sum_{i=0, j=i+\Delta t}^{F \times \frac{1}{f.r.}} \left(x_j - x_i\right)^2 + \left(y_j - y_i\right)^2 \tag{1}$$

Where F = total number of frames, Δt = time interval, and f.r. = frame rate. Mean averages of the squared displacement were taken over 50 particles to ensure an accurate average representation of particle motion. The MSD's were then converted from pixels to μm^2.

Chemotaxis experiments of silica-manganese oxide rods

Chemotaxis was performed in a Dunn chemotaxis cell[2] obtained from Hawksley medical and laboratory equipment. Imaging was performed with a Leica DM2500M optical microscope, using a 40x ph2 objective. Videos were captured with a Nikon D5100 SLR camera. Briefly, a mixture of Paraffin

wax:Vaseline:Briwax (1:1:1 wt. %) was made up in a beaker and heated to 75°C. Then a solution of hydrogen peroxide (30 vol. %) in water was made up to have 0.75 vol. % fuel. A particle suspension of rods (5mg/mL) was then added to the central well (or a mixture of rods/spheres), whilst the outer well was filled with deionized water. A thick cover slip was seeded with the particle solution, and used to cover the wells and bridge (save for a sliver of outer well which was left uncovered). It is essential to make sure no air bubbles are present. Once in place the wax mixture was applied with a paintbrush to seal the coverslip in place and ensure there was no convection from the edges of the coverslip. Then the deionized water was drained from the outer well via the exposed slit to the outer well, and replaced with the hydrogen peroxide solution. The gap that was left in the outer well was then sealed with the wax mixture and imaging performed.

Additional EDAX data

To verify our EDAX data we repeated the measurement on some particles that have not been selectively centrifuged (**Table S1**/ **Figure S1**). These results correlate well with the data included in the main article, however there does appear to be some variation in the manganese oxide content of the catalyst engine.

Ring number	Weight % Mn_2O_3	Weight % SiO_2	Total weight %
1	9.8	90.2	100
2	19.5	80.5	100
3	1.9	98.1	100
4	3.3	96.7	100
5	2.0	98.0	100
6	1.0	99.0	100
7	19.4	80.6	100

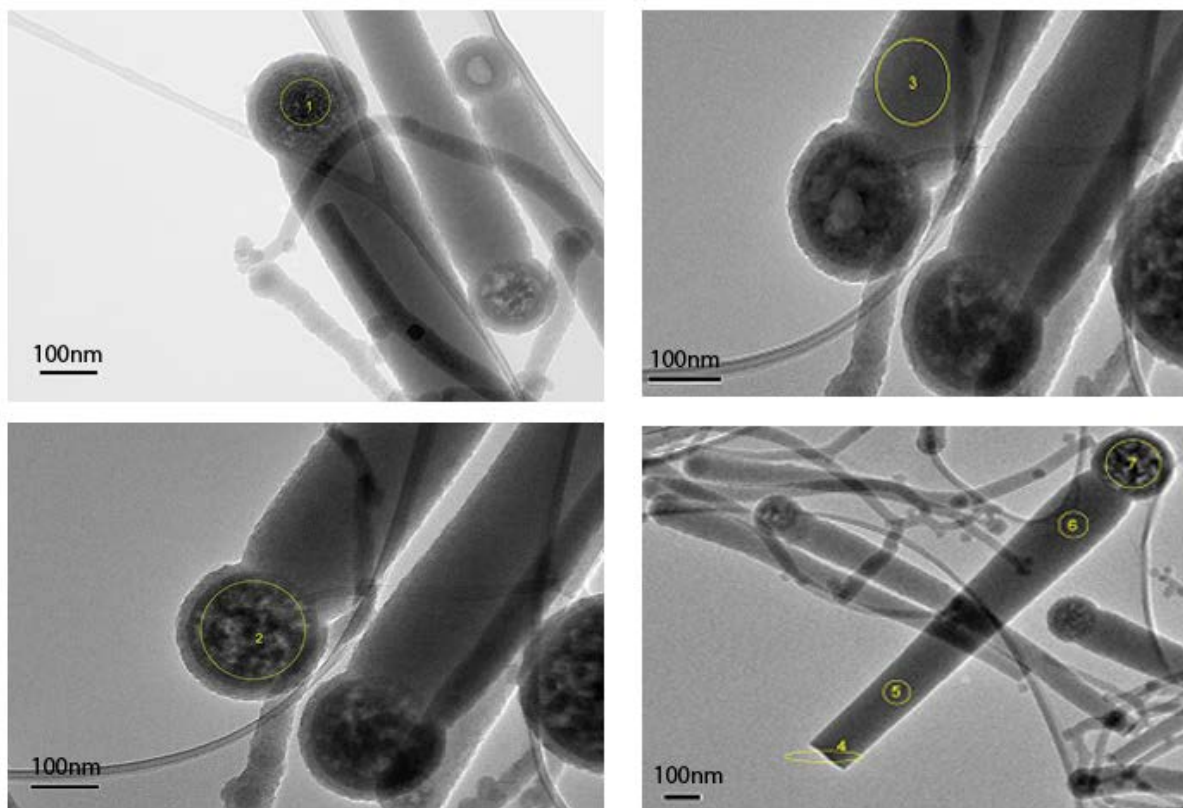**Table S1.** EDAX data for **Figure S1**.

Figure S1. TEM Images with corresponding EDAX analysis locations listed in **Table S1**.

XRD Analysis at elevated temperature

No crystallinity is observed below 800°C for the manganese oxide or silicon oxide phases, however crystallinity is induced above this temperature as can be seen from the plot of scattering intensity as a function of temperature (**Figure S2**). XRD pattern of the sample calcined in air at 850°C shows it to be predominantly crystalline silicon oxide (some hydrated), and a complex mixture of manganese oxides, including Braunite-1Q, Syn which is a mixture of all three elements (**Figure S3**).
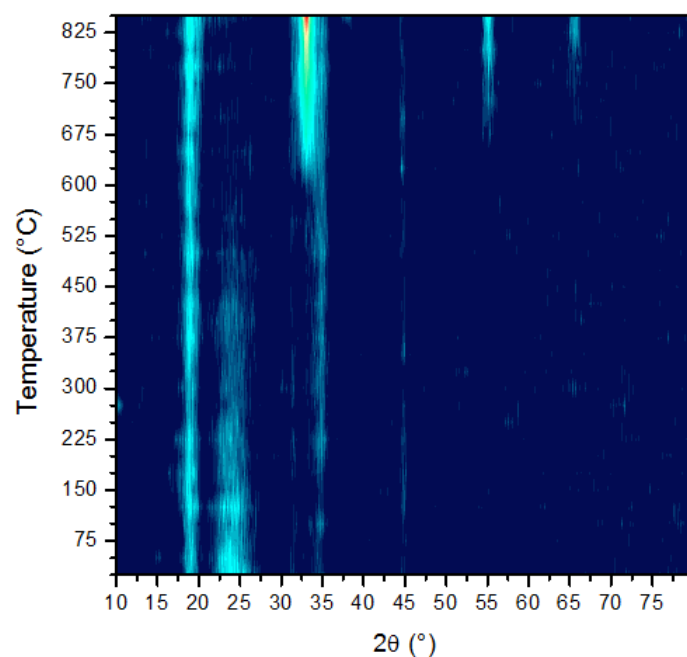
Figure S2. Plot of scattering angle intensity as function of temperature, showing the onset of manganese oxide crystallinity only above 800°C.
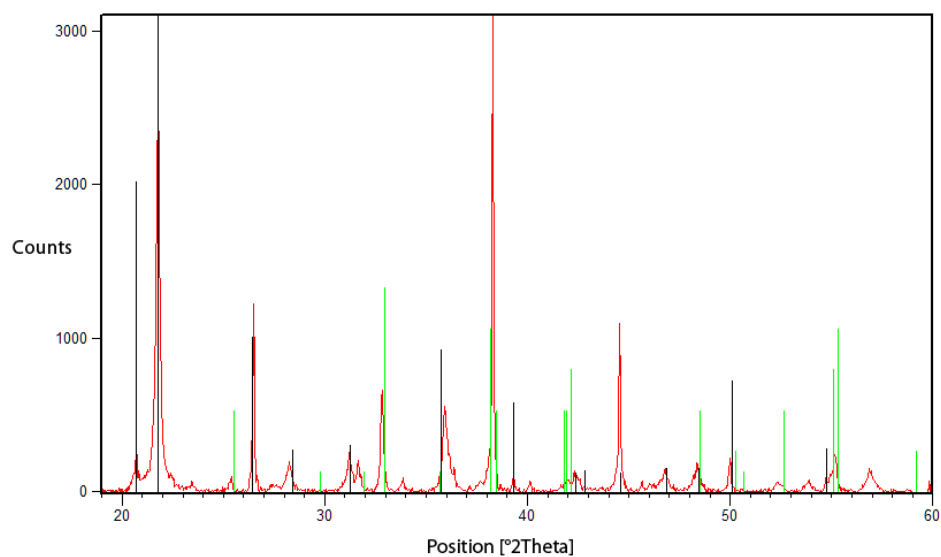

Figure S3. XRD Pattern of silica-manganese oxide rods following calcination in air at 850°C (Red trace). Crystallized forms of silicon oxides could be assigned, namely Opal-A ($SiO_2.xH_2O$) and silicon oxide (SiO_2) - (Black trace). The best fit for the manganese oxide species was Braunite-1Q, Syn (Mn_7SiO_{12}) – (Green trace).

Particle Tracking Data

By looking at the particle traces at different concentrations of hydrogen peroxide (**Fig. S4 A-E**), we can qualitatively rule out propulsion due to convection or sedimentation as the trajectories follow a random walk type of motion. That is there is no overarching directionality in the movement of the particles, which one would expect in the absence of a fuel gradient.
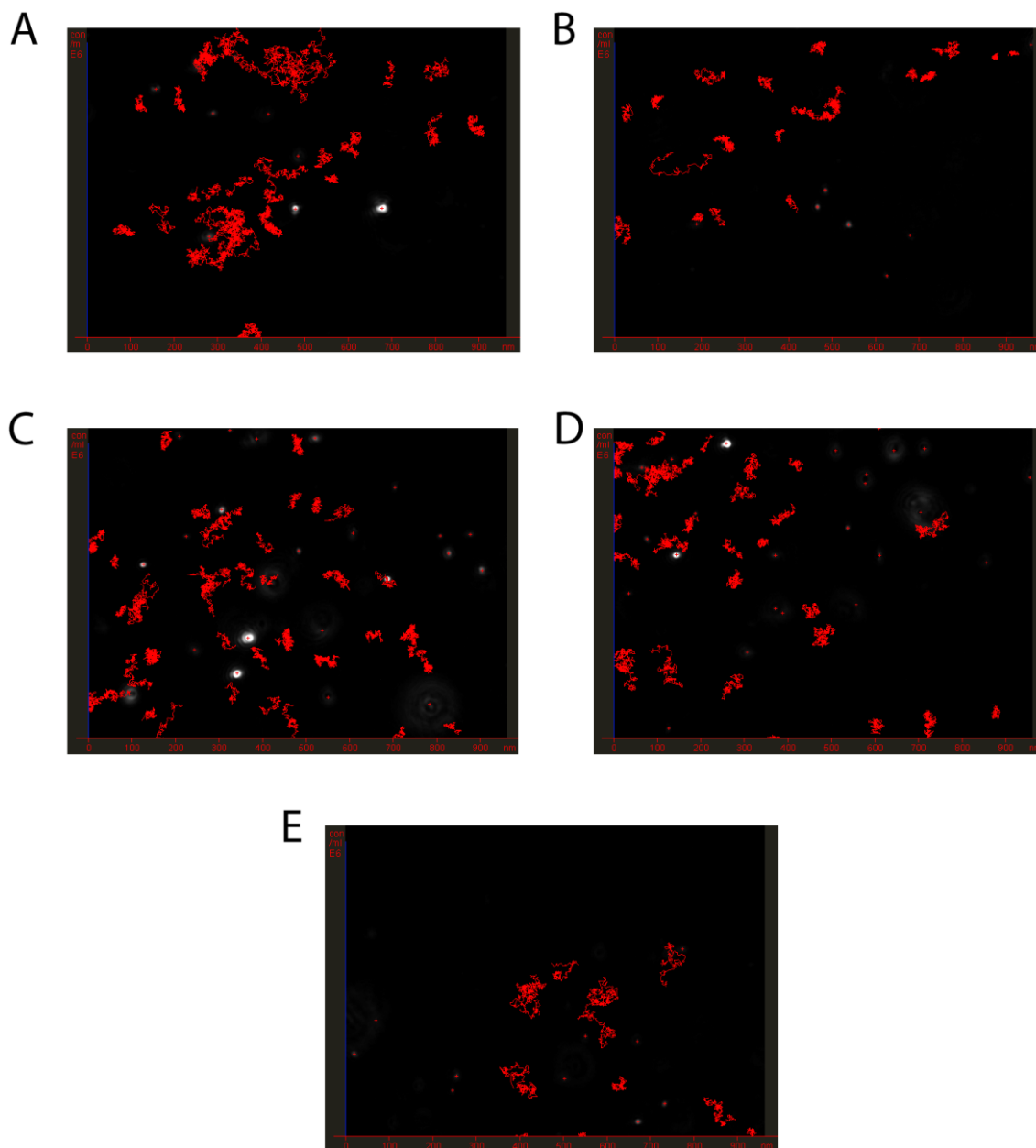

Figure S4. Particle traces for some of the particle trajectories analysed from the particle tracker. H2O2 volume percentages in aqueous phase were (**A**) 0%, (**B**) 0.20%, (**C**) 0.40%, (**D**) 0.60%, and (**E**) 0.80%.

Comments on error analysis in particle tracking

Calculated mean squared displacements for each time interval do not have a normal distribution, making error analysis through calculation of the standard deviation, or margin of error at confidence levels, inapplicable. Similarly it would be invalid to transform the data to a normal distribution, calculate the error, and then invert the transformation function. Instead we have plotted the mean with upper and lower error bars corresponding to the 75th and 25th percentile respectively. In this way we eliminate some of the more extreme outliers due to both polydispersity of the sample and the fact that motion is in fact in 3D in the cell, as opposed to the observed 2D traces. This problem is also compounded at longer time intervals, especially seeing as there are less data points at larger time intervals than at short. From the plot of 0% H_2O_2 and 0.8% H_2O_2 (Figure X blue and red plot respectively) we can deduce a couple of things. Firstly, although there is overlap between the mean squared displacements at the two concentrations, the majority of particles in the presence of a higher concentration of fuel are above the 75th percentile of particles in the absence of fuel, confirming that enhanced diffusion is occurring. Secondly, we can see that the range of mean squared displacements is larger in the presence of fuel than in its absence - possibly due to a magnification of the previously mentioned effects of polydispersity and 3D motion combined with a greater range of displacements possible.
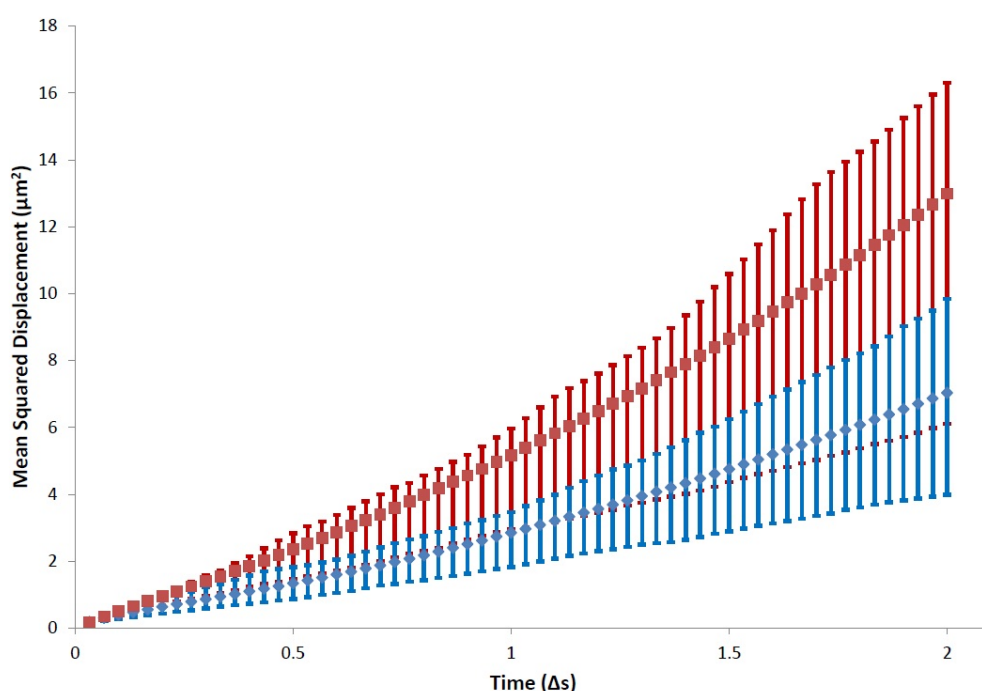

Figure S5. Mean squared displacement as a function of time interval for particles both in the absence of fuel (blue plot), and in the presence of 0.8 Vol. % of H_2O_2. The upper and lower bounds correspond to the 75th and 25th percentile.

Optical Microscopy

A series of optical microscope images at 10x magnification showing a dilute solution of silica-manganese oxide particles (5mg/mL) after the addition of 5 vol. % H_2O_2. Images A-E correspond to 1,2,3,4, and 5s respectively, whilst image F corresponds to 15 seconds (**Figure S6**).
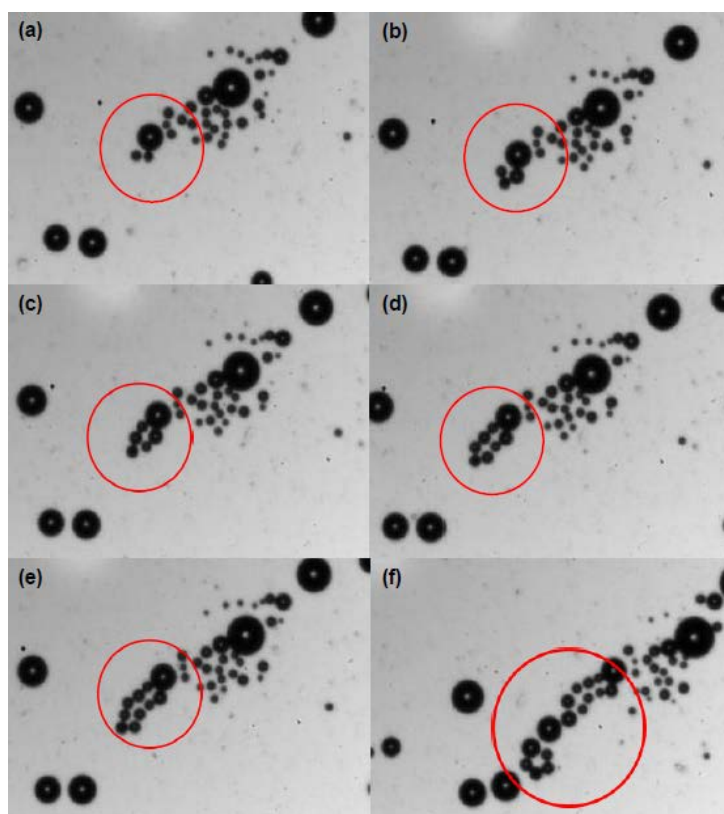

Figure S6. A series of optical microscope frames showing the evolution of oxygen bubbles and water after addition of H_2O_2 (5 Vol. %) to a dilute solution of particles at (a) 1s, (b) 2s, (c) 3s, (d) 4s, (e) 5s, (f) 15s.
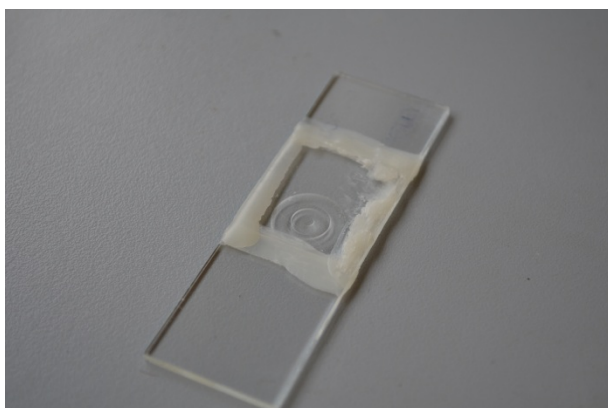
Dunn Chemotaxis Cell

Figure S7. Image of a wax-sealed Dunn cheomtaxis cell. Chemoattractant is placed in the outer well, particle solution is placed on the inside well and seeded onto the cover slip. Imaging is then performed across the bridge region.
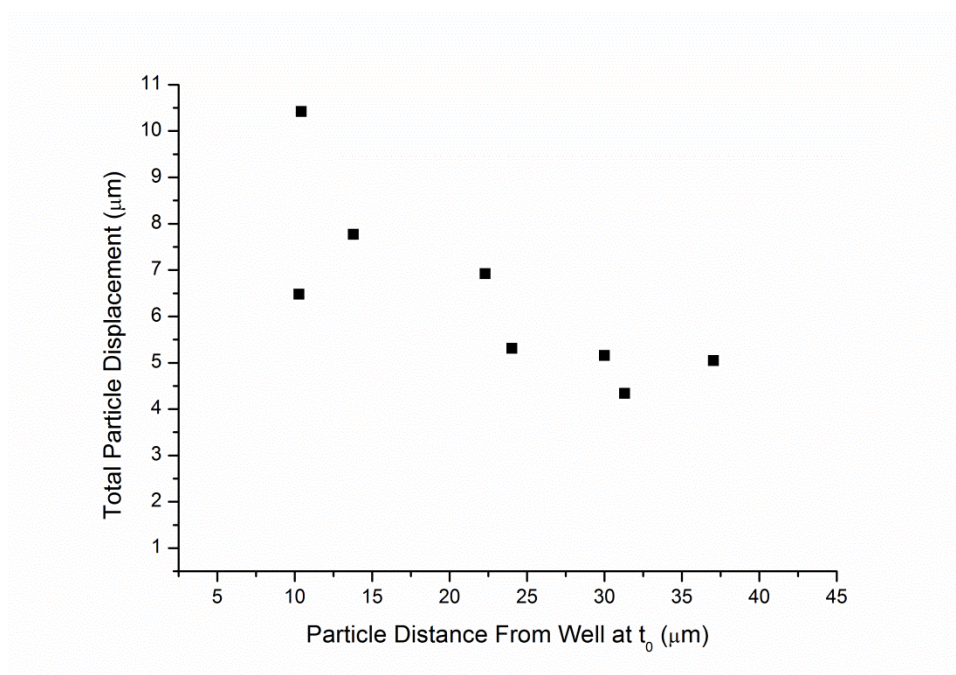

Figure S8. Total particle displacement in the direction of chemotaxis as a function of the initial particle distance from the tangent to the well. Distances were measured from the centre of the particle to the well tangent line.
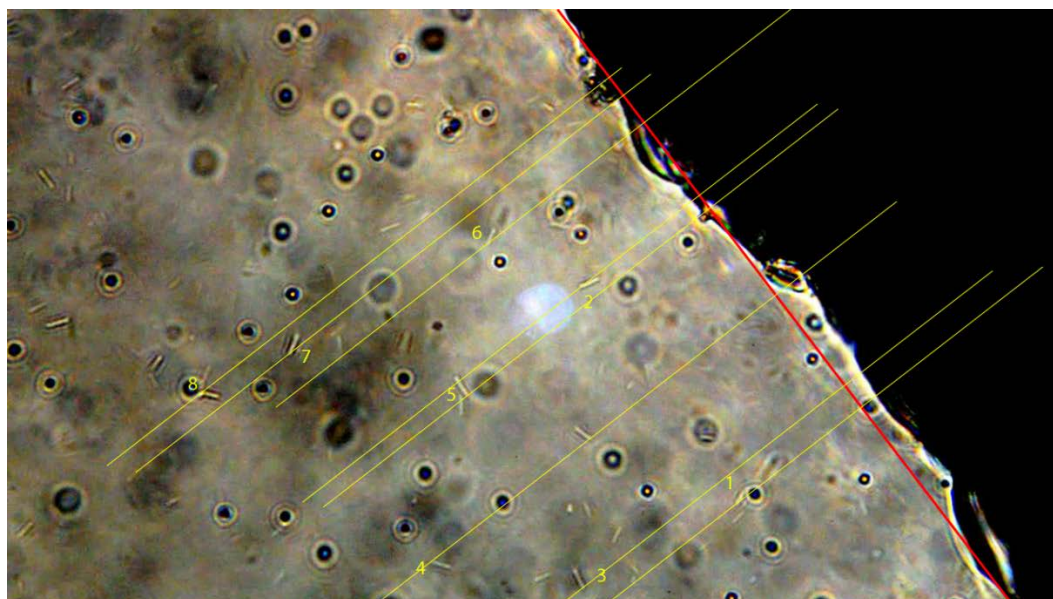
Figure S9. Schematic for how the particle orientation was determined during the chemotaxis experiment. A total of 8 particles were tracked over 10 frames, from t_0 to 90 seconds at 10 second intervals.

References

(1)   Kuijk, A.; Van Blaaderen, A.; Imhof, A. *JACS* **2011**, *133*, 2346–2349.

(2)   Wells, C. M.; Ridley, A. J. *Methods Mol Biol* **2005**, *294*, 31–41.

(3)   Klopfenstein, D. R.; Vale, R. D. *Mol. Biol. Cell* **2004**, *15*, 3729–3739.