Supporting Information for Non-monotonic Speed-dependence of Microswimmers on Wall Distance

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1. Materials and Methods

1.1. Chemicals

Oligo(ethylene glycol)methyl ether methacrylate (OEGMA) and (Hydroxyethyl)methacrylate (HEMA) were purchased from Merck and used without further purification. 2-bromo-2-methyl-N-(3-(triethoxysilyl)propyl)propanamide (BTPAm) and (11-(2-bromo-2-methyl) propionyloxy)- undecyl trichlorosilane (BMPUS) were synthesized according to literature procedure. To prepare the Janus particles, polystyrene particles were initially coated with a 5 nm layer of chromium to enhance the attachment of gold to the particle. Particles were subsequently covered with a 50 nm layer of gold through thermal evaporation technique.

1.2. Synthesis of brush-functionalized substrates

POEGMA synthesis: Glass slides were primarily functionalized with a monolayer of initiator BTPAm. To carry out the polymerization, initiated substrates were immersed into the degassed solution containing 19.4 mL OEGMA (42 mmol) and 22 mL deionized water for 15 minutes, followed by adding 320 mg bipyridine (2.0 mmol) and 82 mg CuCl (840 μmol) and stirring for 30 minutes. Afterwards, the initialized glass slides were immersed into the polymerization solution. The polymerization was terminated after the desired time (15, 30, 45 and 60 minutes) by removing the glasses from the solution and inserting them into ultrapure water.

PHEMA synthesis: Initiation step was achieved by placing glass slides into a solution containing 40 μL BMPUS in 40 mL toluene for 15 h. A polymerization solution of 20 mL HEMA, 20 mL water, 59.4 mg CuCl, 16.14 CuCl2 and 187.42 mg bpy was prepared under nitrogen atmosphere and degassed for 1 h. Then the initiator-deposited glass slides were immersed into the solution and the polymerization was carried out at room temperature for 1, 2, 3 and 4 hours. The termination procedure is similar to the procedure described for POEGMA brush.

1.3. Ellipsometric determination of brush thickness

Ellipsometric measurements were conducted with a polarizer-compensator sample analyzer (PCSA) ellipsometer (Optrel GbR, Sinzing, Germany). The angle of incidence (λ= 632.8 nm) was set to 70° for measurements in ambient conditions and 60° for measurements in water. The data were analyzed by applying a layer model consisting of Si/SiO2/Brush/air (water) to the raw data and upon fitting, refractive index and thickness of the brush layer were obtained.

1.4. Atomic Force Microscopy

Topographical images of the brush-functionalized substrates were obtained by conducting scanning atomic force microscopy in water at room temperature with a Cypher Scanning Probe Microscope from Asylum Research. For scanning in AC mode in water, Olympus AC240TS with spring constant of 2 N/m cantilevers were used. Data were analyzed with Igor program. The root-mean-square roughness σ_{rms} of the scanned area was calculated by using the formula $\sigma_{rms} = \sqrt{\frac{1}{N}\Sigma y_i^2}$ where N is the number of pixels in the scanned area and yi is the z value of the specific pixel. The reported roughness was calculated by taking the average value of 5 measurements at various spots on the sample with scanned area of 1 μm^2.

1.5. Contact Angle Measurements

The advancing water contact angle on the brush substrates was determined with OCA 20 (Dataphysics, Germany). th results are shown in Figure S1. Samples were placed on a stage in a closed cell filled with water to achieve a saturated atmosphere prior to the measurement. 4 μl drop of water was placed via a syringe on the sample. The contact angles were determined by using the tangent fitting method. The measurements were made at different spots on each substrate and the average of these values was determined.

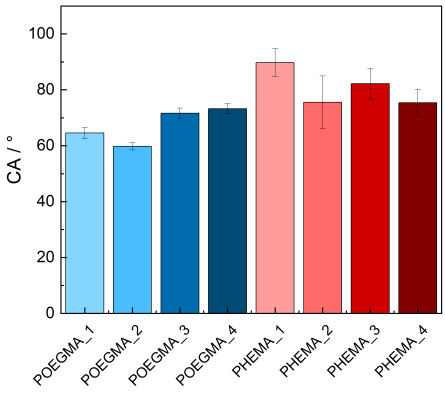

FIG. S1: Water contact angle of the brush-functionalized substrates.

1.6. Preparation of Au-PS Janus particles

A cover slip glass was cleaned with acetone, ethanol, and Milli-q water and further treated with an oxygen plasma for 2 minutes. 10 mol of polystyrene (PS) particles with diameter of 2.4 m was spin-coated on the glass at 8000 rpm for 30 seconds. Afterwards, a 5 nm layer of chromium followed by a 50 nm layer of gold was deposited on the PS particles by vacuum evaporation. Chromium is added to enhance the adhesion of gold to the particles.

1.7. Zeta Potential Measurements

Zeta potential of the Janus particles were determined by using the Zetasizer nano series Nano-Zs (Malvern Instruments, UK) at room temperature.

2. Sample preparation for self-propulsion measurements

To prepare the cell for the self-propulsion tests 0.5 μL of the dispersion of Au-PS particles with diameter of 2.4 μm in water was deposited between two bare/brush-functionalized glass slides. The edges of the glass slides were covered with silicon paste as a spacer. The presence of a spacer is inevitable in order to keep the movement of particles in 2D, as well as to prevent the evaporation of water inside the cell. The distance between two the substrates is roughly 10 m. The cell was placed on top of the objective. Self-propulsion tests were started by introducing the laser in to the system.

3. Dark-field Setup

The experimental setup is schematically shown in Figure 1a. It consists of a dark-field condenser (Olympus NA 1.2-1.4) to achieve a greater detection of the gold cap of particles. The scattered light of the particles is collected by an oil-immersion objective (Olympus 100x, adjustable NA 0.5-1.35) and imaged by a sCMOS camera (ANDOR, ZYLA

4.2). Laser (Pegasus, Pluto, 800 mW) with the wavelength of 532 nm is coupled to the microscope. In order to achieve a wide parallel beam at the objective, the laser beam passes through a beam expander (Thorlabs, 5-10x, 350-650 nm) and a lens subsequently. Beam expander widens the beam diameter and the lens focuses the beam to the back focal plane of the objective. As a result, a wide parallel laser beam is formed at the objective, Figure 1b. An important aspect of the setup is the presence of a nano-positioning stage (P-545.2R7), by which placing the microscope stage on nano-scale is achievable. Upon illuminating the sample cell with various laser intensities the position of the particle in every frame is obtained, and once the particle is out of the illumination area the information will be given to the nano-positioning stage through a feedback loop and it will move itself such that the particle is again in the center of illumination.

4. Trajectories and MSD Curves

Trajectories, MSD curves, and the diffusion coefficients of the Au-PS Janus particles are shown here.

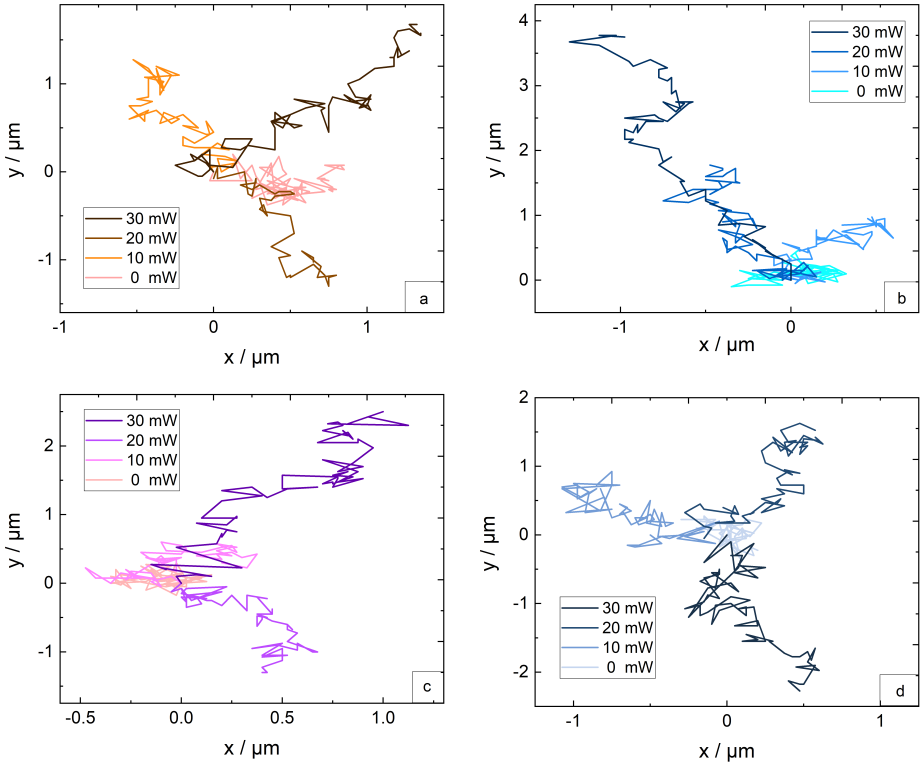

FIG. S2: Trajectories of Au-PS Janus particles near a) PHEMA-1, b) PHEMA-2, c) PHEMA-3, d) PHEMA-4 under various laser intensities within 2 seconds.

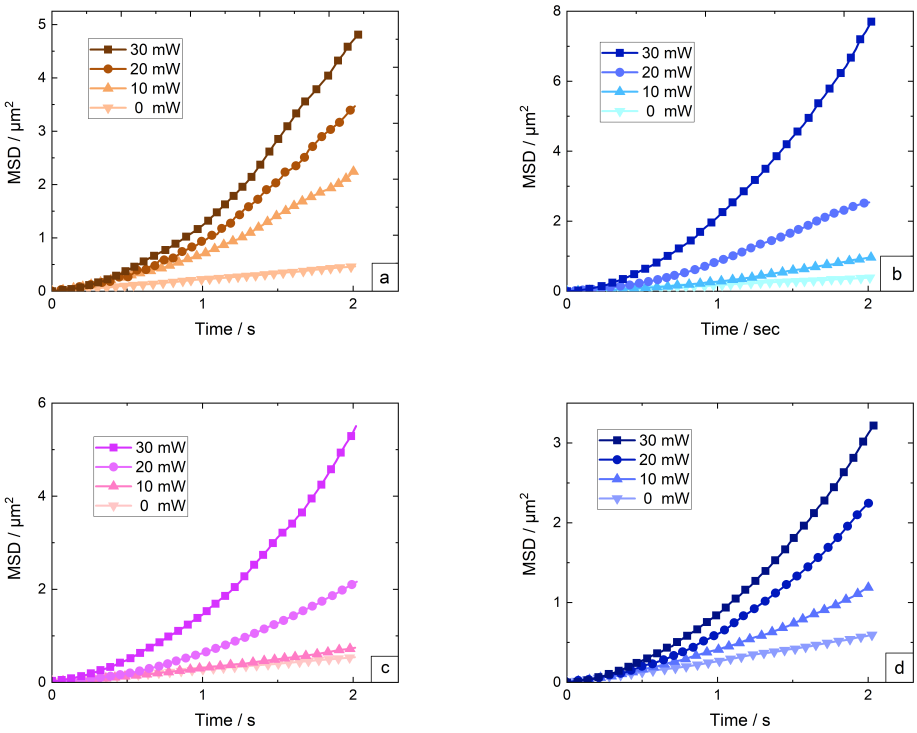

FIG. S3: Mean-squared-displacement of Au-PS Janus particles near a) PHEMA-1, b) PHEMA-2, c) PHEMA-3, d) PHEMA-4 under various laser intensities.

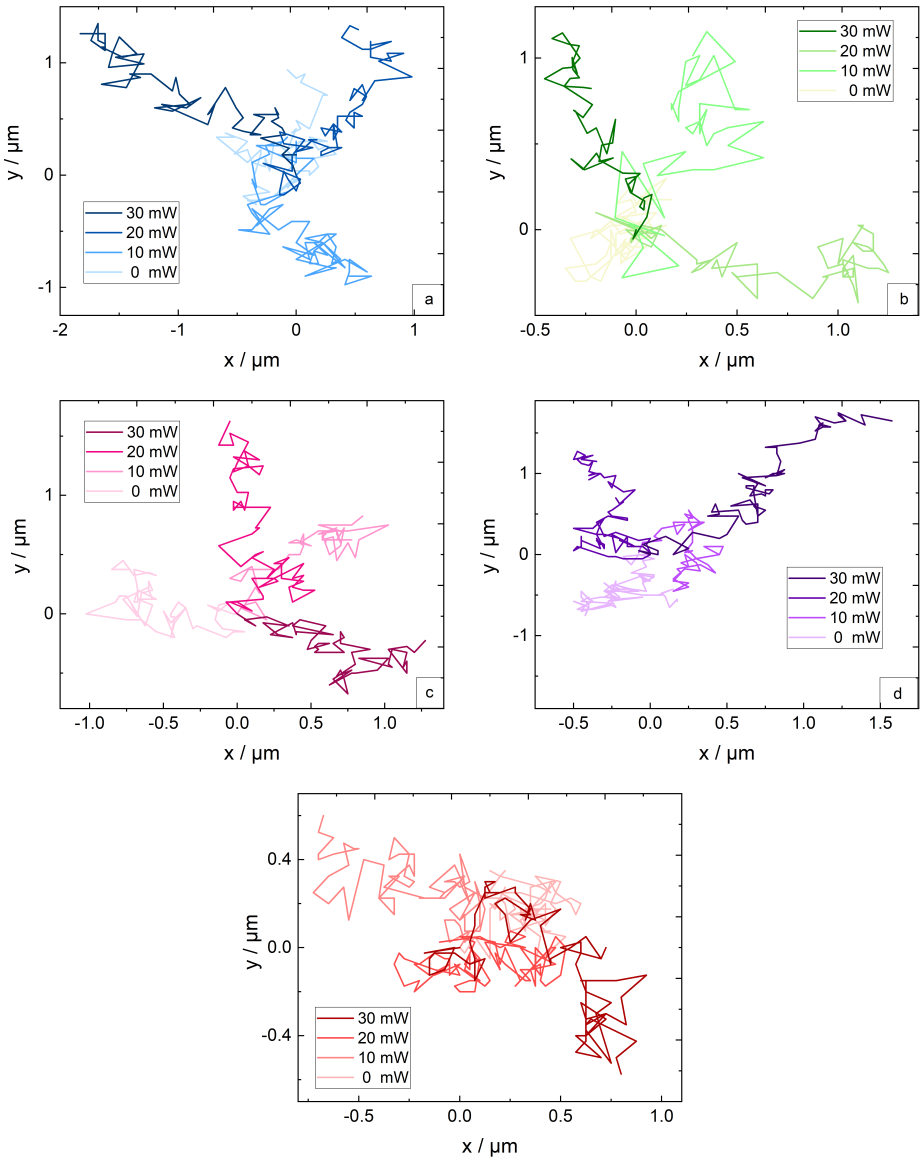

FIG. S4: Trajectories of Au-PS Janus particles near a) POEGMA-1, b) POEGMA-2, c) POEGMA-3, d) POEGMA-4, and e) bare glass under various laser intensities within 2 seconds.

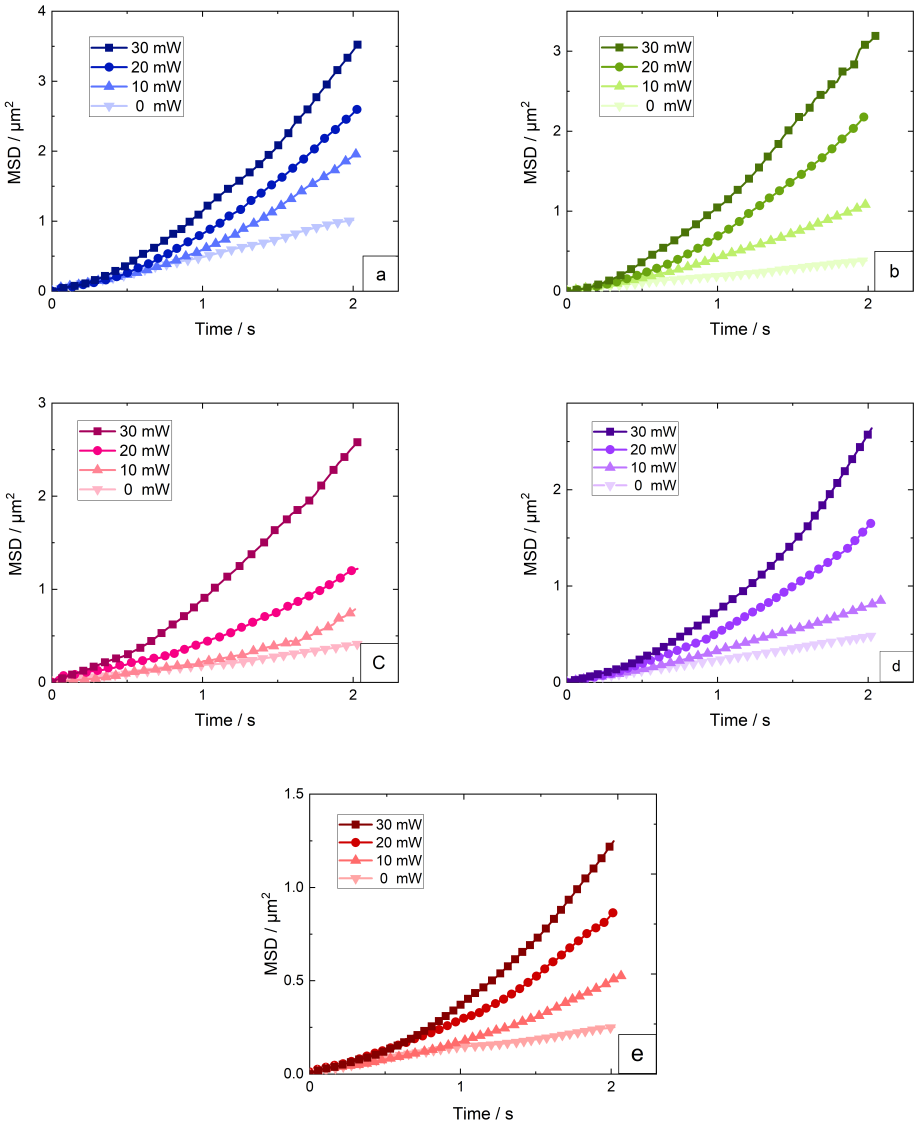

FIG. S5: Mean-squared-displacement of Au-PS Janus particles near a) POEGMA-1, b) POEGMA-2, c) POEGMA-3, d) POEGMA-4, and e) bare glass under various laser intensities.

5. Diffusion coefficients of the Au-PS particles

The dashed lines in Figure S6 represent the diffusion coefficient of the Au-PS Janus particles in bulk, using $D_{\text{bulk}} = \frac{k_B T}{6\pi\eta R}$, where k_B is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the solvent, and R is the particle radius. The reduced diffusion coefficient $\frac{D}{D_{\text{bulk}}}$ is roughly 0.45, which is in agreement with literature.[1]

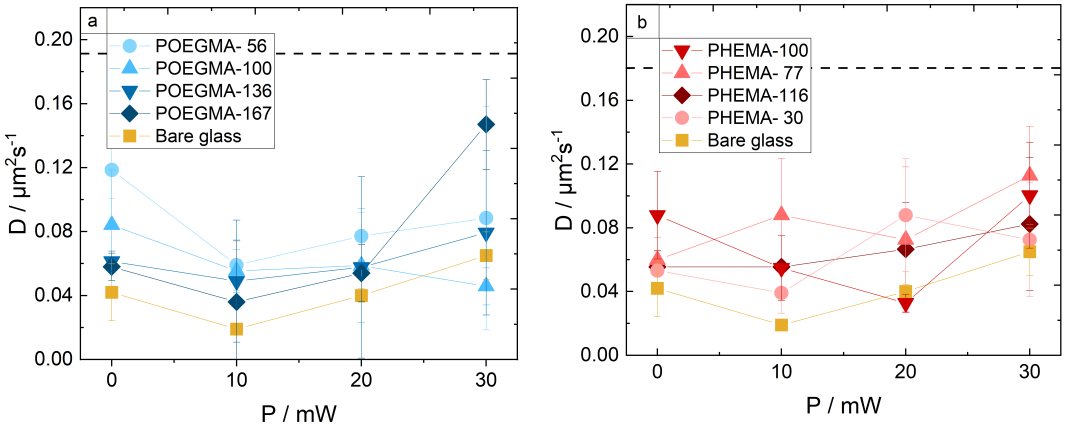

FIG. S6: Diffusion coefficients of Au-PS Janus particles near a) POEGMA, b) PHEMA brush functionalized substrates; The dashed line represents the diffusion coefficient of the particle in bulk, D_{bulk}.

[1] S. Ketzetzi, J. de Graaf and D. J. Kraft, *Physical Review Letters*, 2020, **125**, 238001.