Microswimmers from Toposelective Nanoparticle Attachment

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Microswimmers hold promise for applications ranging from targeted delivery to enhanced mixing at the microscale. However, current fabrication techniques suffer from limited throughput and material selection. Here, a versatile route enabling the synthesis of microswimmers from off-the-shelf micro- and nano-particles is demonstrated. The protocol hinges on the toposelective attachment of photocatalytic nanoparticles onto microparticles, exploiting a multi-functional polymer and a Pickering-wax emulsification step, to yield large quantities of photo-responsive active Janus particles. The polymer presents both silane and nitrocatechol groups, binding silica microspheres to a range of metal oxide nanoparticles. The Pickering-wax emulsions protect part of the microspheres’ surface, enabling asymmetric functionalization, as required for self-propulsion. The resulting photocatalytic microswimmers display a characteristic orientation-dependent 3D active motion upon ultra-violet illumination, different from that conventionally described in the literature. By connecting the extensive library of heterogeneous nanoparticle photocatalysts with the nascent field of active matter, this versatile material platform lays the groundwork toward designer microswimmers, which can swim by catalyzing a broad range of chemical reactions with potential for future applications.

1. Introduction

Machines increasingly perform tasks once believed the prerogative of biological systems. Yet, advances in automation are mostly limited to large machines such as cars, drones, and industrial robots. The advent of microswimmers, artificial objects that can convert energy sources such as light or chemicals into directed motion,\(^1\) promises to bring automation down to the micro- and nano-scale. Microswimmers can transport matter at the microscale and induce the mixing and pumping of fluids without external agitation,\(^2\) thus offering tantalizing opportunities for performing autonomous tasks at small scales in applications ranging from targeted drug delivery,\(^3\) to environmental remediation,\(^4\) and even energy conversion.\(^5\) However, significant technological hurdles must first be overcome if microswimmers are to realise their potential for real-world applications.

Fabrication remains perhaps the most significant challenge to applied active matter, as both top-down and bottom-up approaches demonstrate significant limitations with respect to scalability and modularity in combining different materials.\(^6\) Designing novel multi-functional micromachines requires increasingly expensive and specialized equipment, for example, for two-photon polymerization,\(^7\) with implications for the accessibility of scientific research.\(^8\) In contrast to the complex micromachines produced by such techniques, Janus microswimmers are arguably the simplest class of synthetic active matter. These rely on surface patches with different physicochemical (e.g., catalytic) properties for propulsion in self-generated gradients.\(^8\) In fact, Janus-structured catalysts are of general research interest as a means to obtain advanced biphasic reaction media via Pickering emulsions\(^9\) (e.g., for Pickering interfacial catalysis\(^10\)), and for the opportunities they provide to engineer heterojunctions\(^11\) to design more efficient photocatalytic materials with enhanced electric field localization and reduced charge recombination. Returning to their use in active matter, Janus catalytic swimmers do not need external actuation, and only require a chemical fuel source to move. Nevertheless, even this simple material platform typically suffers from a very low fabrication throughput due to the methodology used to produce the surface patches.\(^12\)

Janus microswimmers are typically produced by sputter-coating particle monolayers, exploiting line-of-sight vapour-phase deposition and particle self-shadowing.\(^6\) Metal coatings are thus selectively deposited as a spherical cap, whose extension can be controlled by tilting the monolayer.\(^13,14\) Despite its widespread popularity, this approach has clear downsides, namely a yield on the order of micrograms and a highly inefficient use of metal precursors. A notable exception to this trend in active matter synthesis, which demonstrated both scalability and avoided the use of inorganic catalysts, can be found in the work of Simmchen et al.,\(^15\) who first demonstrated the use of Pickering wax emulsions to obtain nanomotors powered by catalase. The combination of biological catalysts with artificial materials to obtain biohybrid micro- and nanorobots has garnered significant attention in recent years.

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with proposed biomedical applications.[16] Regarding more conventional chemical microswimmers, Archer et al. demonstrated the scalable fabrication of metal-catalyst functionalized Janus microswimmers via Pickering-wax emulsions using a two-step nanoparticle seeding and film-growth protocol.[17] However, the technique they describe is specific to platinum and does not provide close control over the film morphology or composition. The constrained material and synthetic options in the literature, although inconsequential for fundamental studies, hamper the progress of applied active matter and, in particular, inhibit the development of propulsion mechanisms based on useful chemical reactions.

Here, we demonstrate a modular approach to achieve the asymmetric functionalization of microparticles from the toposelective attachment of different nanoparticle thin films, thereby obtaining large (>100 mg) quantities of photo-responsive Janus microswimmers. The fabrication of catalytic Janus structures using the Pickering wax emulsion technique has in particular been well-established, among others, by Szynkiewicz and co-workers, who have demonstrated the asymmetric growth of metal nanoparticles from solution onto sub-micron SiO₂ supports[18,19] to obtain Janus particles with properties advantageous for interfacial catalysis. The “hairiness” of the stimuli-responsive poly(acrylic acid) matrix containing the metal nanoparticles also increases their accessible surface area, and thus catalytic efficiency. In this work, we extend this approach and its scope by utilizing pre-synthesized industrial metal-coordination chemistries through the introduction of various functional groups. Focusing on commercial TiO₂ P-25 not bound to the SiO₂ surface.

The produced P-25/SiO₂ microparticles are imaged using scanning electron microscopy (SEM). We find that in the literature, although inconsequential for fundamental studies, the technique they describe is specific to platinum and does not provide close control over the film morphology or composition. The constrained material and synthetic options in the literature, although inconsequential for fundamental studies, hamper the progress of applied active matter and, in particular, inhibit the development of propulsion mechanisms based on useful chemical reactions.

2. Results and Discussion

2.1. Polymer-Assisted Nanoparticle Attachment on Microspheres

The first step in the fabrication of our photocatalytic microswimmers is to identify a protocol for the robust attachment of nanoparticle thin films onto the microparticle supports. Electrostatic attachment is frequently used as a means for colloidal heteroaggregation; however, it cannot withstand the harsh cleaning protocols required to remove the solidified wax in Pickering-wax emulsions. Alternative strategies employing covalent bonds are therefore to be sought. In particular, silane groups are frequently used as anchors for SiO₂, while a raft of coordination chemistries exist for transition metal complexes. However, combining all these features into a single, facile, and robust protocol presents significant challenges. Here, we overcome these obstacles by means of a polymer bridge. This comprises an acrylamide polymer backbone functionalized with both nitrocatechols and silanes to provide multiple covalent linking sites that can stably bind the nanoparticles to the SiO₂ surface.

We base our polymer bridge on (poly)pentafluorocarboxylate (pPFPCAC), a post-modifiable polymer containing reactive ester linkages, which can be exchanged with amine-containing functional groups by nucleophilic substitution. To decorate our microparticles with various metal-oxide nanoparticles, we functionalize this pPFPCAC backbone with: i) N-boc-hexanedi-amine, ii) nitrocatechols, and (iii) silane-based groups to obtain poly(acrylamide)-g-(1,6-hexanediamin, 3-aminopropyl)methoxy silane, nitrodopamine.[20] The N-boc protecting group on the diamine is removed with trifluoroacetic acid (TFA), exposing protonated amines on the polymer backbone. This electrostatic component assists the polymer conformation when binding to negatively charged inorganic surfaces. The silane groups covalently bind the polymer to the SiO₂ microsupport via siloxane groups, while nitrodopamine facilitates chelation to a range of metals, including titanium and iron oxides.[24,25] In this way, the multi-functional polymer acts as a bridge that provides anchoring between the cores of silica microparticles and oxide nanoparticles in a simple heteroaggregation process.

We optimize the attachment of uniform nanoparticle films focusing on TiO₂ P-25 as our benchmark nanoparticle system, in concurrence with its status within the field of photocatalysis. The process, schematized in Figure 1a, starts with the activation of the surface of the SiO₂ microparticles by an initial cleaning step, using a hot ammonia and hydrogen peroxide bath to provide available hydroxyl groups to form siloxane bonds with the polymer. The polymer is first dispersed at varying concentrations at 50°C overnight. Cleaned particles are then added dropwise to the polymer solutions under magnetic stirring, and left to mix overnight at a final concentration of 0.1 W/v%. After stirring, the SiO₂ is then washed by centrifugation with double-distilled water to remove excess polymer from solution. The SiO₂ particles retain a yellow color from the polymer, due to the presence of nitrodopamine. The functionalized polymer-SiO₂ particles are then dispersed in a phosphate-buffered saline (PBS) 70 buffer solution, adapting the protocol of Serrano et al. for flat substrates.[20] The particles obtain a pinkish hue, likely arising from conformational changes of nitrodopamine in alkaline environments.[25] TiO₂ P-25 of varying concentrations is then added dropwise to a stirred 0.1 w% solution of the polymer/SiO₂ microparticles and then left mixing overnight. Finally, the P-25/SiO₂ microparticles are washed extensively with alternating sonication and centrifugation steps to remove any excess TiO₂ P-25 not bound to the SiO₂.

The produced P-25/SiO₂ microparticles are imaged using scanning electron microscopy (SEM). We find that in the
absence of the polymer functionalization step, no TiO$_2$ P-25 nanoparticles are bound to the SiO$_2$ microparticles after washing (Figure 1b), even at the highest TiO$_2$ concentrations investigated. We also verify this with inductively coupled plasma optical emission spectrometry (ICP-OES) elemental analysis, and find negligible quantities of Ti in the sample (Figure 1e).
highlighting the effectiveness of the cleaning protocol and the requirement for the polymer to bind the TiO$_2$ P-25 nanoparticles (Figures 1b–e). The TiO$_2$ loading can be effectively controlled by varying the amount of polymer and TiO$_2$ P-25 added, and is retained after washing (Figures 1e,f). We observe a linear growth in the Ti/Si ratio with increasing polymer concentration (Figure 1e), which is limited by the solubility of the polymer in water. The Ti/Si ratio would naturally saturate with increasing TiO$_2$ P-25 (Figure 1f), but at the highest TiO$_2$ concentrations we explore, aggregation of the nanoparticles starts to occur.

### 2.2. Toposelective nanoparticle attachment

Having established the success of the bulk surface modification, we combine it with a Pickering wax emulsion approach to produce asymmetrically functionalized SiO$_2$ microparticles, en route to realizing photocatalytic microswimmers.[22] This strategy consists in decorating the surface of molten wax droplets in an aqueous medium with SiO$_2$ microparticles. The particles are reversibly adsorbed at the water–wax interface and are immobilized when solidifying the wax upon cooling. The surface of the particles immersed in the wax is then protected from surface modifications that are carried out in the aqueous medium. In particular, we prepare our Pickering emulsions by adapting the methodology described by Perro et al.[26] Cleaned particles are dispersed in didodecylmethylammonium bromide (DDAB) solutions with concentrations corresponding to an approximate surfactant monolayer coverage on all particles. Wax is added to the suspension, which is heated to 75°C, and then subjected to a two-step vigorous stirring protocol (see Experimental Section for more details). The hot emulsion is then rapidly cooled in an ice-bath to obtain solidified SiO$_2$-wax colloidosomes (Figure S1a–d, Supporting Information). The colloidosomes are then washed consecutively by gravitational sedimentation with distilled water, a 0.1 M NaCl solution to remove the DDAB cationic surfactant, then water once more to remove the salt. At this stage, we add the multifunctional polymer to coat the exposed surface of the SiO$_2$ particles. The colloidosomes are dispersed in the polymer solution, gently agitated overnight with an orbital mixer, then washed once more with distilled water to remove excess polymer, redispersed in a pH 7.0 PBS solution, and gently mixed with the nanoparticles overnight. Finally, the colloidosomes are collected and dried, before mixing and filtering with chloroform to remove the wax (Figure 1g).

For straightforward functionalization of the colloidosomes, they should be denser than water (Figure S3, Supporting Information). Colloidosomes with a mean diameter of 33.4 μm are produced using 2.12 μm particles (Figure S2, Supporting Information). A particle concentration of 5 w/v% in water is emulsified with wax in a 1:10 wax:water volumetric ratio. The process can be readily tuned to produce colloidosomes with SiO$_2$ particles of varying sizes (Figure S1a–d, Supporting Information). Microparticle size provides a convenient handle on controlling physical properties of the final microswimmers such as the diffusion rotation coefficient, which could be exploited for, for example, enhanced mixing[31] or navigation.[32] However, unlike some previous reports, we were not able to tune particle penetration into the wax with surfactant concentration—instead we found that the surfactant concentration only determined whether or not it was possible to obtain Pickering emulsions.[26]

Our process gives an approximate 50–50 TiO$_2$/SiO$_2$ surface coating (Figure 1i–k). Ti loading is also confirmed by ICP-OES, which gives an approximate 50% coverage for the Janus microswimmers, as observed with SEM (Figures 1e,f). The value contrasts with the expected nanoparticle coverage based on the penetration of the SiO$_2$ microparticles into the wax (approximately 0.36R from direct measurement of the three-phase contact angle) and on previous findings using Pickering-wax emulsions.[27,28] We hypothesize that the closely packed monolayers of SiO$_2$ form an effective barrier to the transport of TiO$_2$ P-25 nanoparticles onto the whole surface of the silica particles that is not protected by the wax, thereby preventing a higher surface coverage. The rotated particles in Figure 1i, likely a result of subsequent filtration steps after nanoparticle attachment, also suggest this shadowing effect. The Janus morphology is retained after the harsh cleaning protocols necessary to remove excess nanoparticles and wax, and the redisursal of the dried Janus microswimmers in water (Figures 1j,k), indicating the durability of the polymer linkage. We note that the density of the nanoparticle films obtained in the asymmetric case visually appears to be slightly lower than in the symmetric one. This slight reduction may be due to a combination of processing factors, including the gentler agitation process used to functionalize the colloidosomes, the reduction in the electrostatic driving force present in water during dispersal in chloroform, which likely contributes to the attachment of TiO$_2$ to the positively charged polymer, possible contamination from dissolved wax in the chloroform, and the high shear rates applied during the two filtration steps which could remove some nanoparticles. However, quantitative analysis by ICP-OES shows that the reduction in the Ti loading from that expected for 50% coverage is minimal.

We confirm the Janus distribution of TiO$_2$ by elemental mapping, namely high-angle annular dark-field imaging energy-dispersive X-ray spectroscopy (HAADF-EDS) (Figures 2a–c). Using transmission electron microscopy (TEM), we are able to visualize the morphology of the thin nanoparticle films. The thin films are networks of attached nanoparticle clusters formed from multiple TiO$_2$ primary particles rather than individual nanoparticle structures. This is in agreement with the expected morphology of commercial TiO$_2$ P-25.[33] The formation of such porous nanoparticle structures is favorable due to their enhanced surface area compared to dense films,[34] thereby increasing catalytic activity and thus swimming speeds.[35]

Utilizing nitroacetate chelation chemistry extends the applicability of our polymer-based nanoparticle attachment to a range of metal oxides, and could therefore be exploited to obtain composite thin films of functional nanoparticles on microparticle supports. To this end, and to demonstrate the generality of our method, we also attach different phases of TiO$_2$ (amorphous, anatase, and rutile), Fe$_2$O$_3$, and SrTiO$_3$ using the same protocols developed for TiO$_2$ P-25 (Figure 3). We note that we did not optimize the dispersion of the different nanoparticle systems, which in turn affected the coverage on the SiO$_2$ supports. Developing protocols to obtain uniform composite thin films incorporating various functional nanoparticles will be the focus of future work. Fe$_2$O$_3$ imparts both photocatalytic and magnetic properties, and could be combined...
To investigate the autonomous, photocatalytic motion of our TiO$_2$ P-25 microswimmers, we perform single-particle tracking studies with bright-field microscopy, using in-house particle-tracking scripts under different illumination conditions and H$_2$O$_2$ concentrations. We additionally briefly examine the effect that the phase of TiO$_2$ nanoparticles used has on swimming speeds. TiO$_2$ is known to degrade H$_2$O$_2$ under UV light, and the Janus distribution of TiO$_2$ P-25 nanoparticles on the SiO$_2$ core’s surface thus leads to the formation of asymmetric gradients around the microswimmers. These in turn develop flow fields which result in self-phoresis of the particles (Figure 4a,b). We first confirmed the photo-responsive behavior of the microswimmers by alternating off-on UV illumination cycles and found that the UV illumination is a necessary pre-condition for motion (Figure 4c,d), with no evidence of memory or photo-charging effects. We then evaluated the instantaneous velocities of the microswimmers under different illumination strengths and wavelengths (Figure S8, Supporting Information).

The trajectories of microswimmers are typically described with a 2D active Brownian motion model, where a constant propulsion velocity is randomized in 2D by rotational diffusion. More recently, there has also been a focus on fabricating and studying microswimmers with unbounded 3D active motion. However, our microswimmers demonstrate more complex behavior, which does not follow the 2D and 3D active Brownian motion equations. Specifically, their motion is mostly confined to the 2D plane, with interdispersed short and rapid periods of out-of-plane motion (Figures 4c,h; Video S3, Supporting Information). The predominantly 2D motion may be explained by hydrodynamic interactions with the glass substrate, which favor in-plane motion. Competing effects from out-of-plane rotational diffusion and angular velocity arising from a non-uniform nanoparticle coating and wall-induced flow could cause the observed random out-of-plane ballistic segments. To characterize this 3D motion, we first confirm that in the absence of chemical fuel the particles are able to rotate in 3D (Video S2, Supporting Information) and measure their rotational diffusion in solvents of varying viscosity in line with theory (Table S1, Supporting Information). We then measure their 3D active trajectories via a simple approach making use of the changing diffraction patterns of the particles as they swim in and out of the focal plane (see Text S3, Supporting Information, for details).

From the analysis of individual 3D trajectories, like the one reported in Figure 4e, we measure median instantaneous velocities ranging from 2–13 μm s$^{-1}$ on a per particle basis, and note that the particles swim cap first (Figure 4a; Video S1, Supporting Information). Under the conditions found to maximize swimming speeds (3 v% H$_2$O$_2$, 340 nm, 9.4 mW mm$^{-2}$), we find a median instantaneous velocity of approximately 6.5 μm s$^{-1}$ on a per particle basis (Figure S8, Supporting Information). Lowering the fuel concentration leads to lower swimming speeds and also note a difference in swimming speed depending on the wavelength of illumination used. Finally, we observe that microswimmers functionalized with amorphous TiO$_2$ nanoparticles, known to be the least catalytically active phase of TiO$_2$, demonstrate significantly lower speeds than the P-25 system, highlighting the importance of photocatalyst selection (Figure S9, Supporting Information).

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By plotting the instantaneous velocities as a function of particle orientation, we observe a significant asymmetry in the particle motion (Figure 4f–h). In particular, the microswimmers exhibit orientation-dependent velocities, displaying faster motion as their orientation is increasingly directed out of plane. The effect persists over multiple frames, indicating that it is not a tracking artifact. Moreover, contrary to
expectations where shadowing dictates particle motion,\cite{48} the observed faster segments are not uni-directional. Furthermore, the previously discussed on-off photo-responsiveness of the particles excludes a memory or charging effect,\cite{40} which might have explained the bi-directional fast swimming segments (Figure 4c,d). Based on the fact that the transmission of 340 nm wavelength light through 2 μm fused SiO₂ is on the order of 90% (even after accounting for Fresnel losses), we hypothesise that the SiO₂ core does not block the UV light. This implies that even when the catalytic cap is completely “shadowed”, upward swimming is observed, and we attribute the fastest motion toward the substrate (cap down) to the direct illumination of the catalytic cap and the concurrent effect of gravity. The slower in-plane motion could be caused by the orientation of the propulsion direction, and the near-wall hydrodynamic interactions which increase drag forces.\cite{49} Although statistics for 2D active Brownian trajectories with orientation-dependent velocities have been reported,\cite{50} their extension to the the 3D case reported here presents potential for future theoretical developments.

Figure 3. Symmetric and asymmetric functionalization of SiO₂ microparticles with various commercial, pre-synthesized nanoparticles, highlighting the versatility of the proposed approach (scale bars 500 nm).

Figure 4. Overview of particle motion under UV illumination in fuel-rich media. a) Schematic of particle motion. Under the decomposition of hydrogen peroxide, the microswimmers swim with the functionalized cap forwards. b) Wide-field image with superimposed trajectories (shown for 3 s, see Video S4, Supporting Information) under UV illumination (scale bar 20 μm). c) Distribution of instantaneous velocities during off (black) and on (violet) cycles. d) Mean instantaneous velocities of particles during alternating of–on cycles of UV illumination. The error bars correspond to confidence intervals, which were obtained with bootstrapping. e) Example of a microswimmer trajectory in 3D, with the magnitude of the velocity vector color-coded to illustrate the occurrence of an orientation-dependent velocity. f) Plot of particle velocity versus out-of-plane orientation angle. Particles swim faster out of plane, and the fastest motion is observed when the particle swims towards the glass substrate from above (θ = -90°). g) Distribution of out-of-plane orientation angles (θ) across all particle trajectories. h) Distribution of displacements for all particles in x, y, and z. The distributions in x and y (in-plane) are Gaussian and similar, while the distribution of z displacements shows pronounced tails.
3. Conclusion

We have demonstrated a modular approach to fabricate large (100 mg) quantities of photo-responsive microswimmers from the asymmetric attachment of commercial nanoparticles. Our method, which hinges on a multi-functional polymeric anchor that can be readily modified to incorporate a range of chemical groups, provides a versatile material platform which can be extended to various functional nanoparticles. We envision that it will offer an “off-the-shelf” modular approach to obtain large quantities of Janus particles with mixed composite films for a range of applications. The described protocol does not require specialized equipment beyond that found in typical synthesis laboratories, lending itself to wide-spread application.

Moreover, the motion of our photo-responsive microswimmers highlights several avenues for further research. Analysis of the observed 3D swimming behaviour requires an extension to the current theoretical framework discussed in the literature. We also note that the TiO$_2$ P-25 microswimmers self-propel more slowly at higher illumination wavelengths, which we attribute to TiO$_2$’s large energy band gap. Furthermore, we observe that the type of TiO$_2$ used to functionalize the microswimmers can have a significant impact on their swimming behavior. This demonstrates the opportunities to exploit the wealth of catalysis literature to inform the design of microswimmers with desirable attributes (e.g., with faster swimming speeds or visible light activation) by appropriate selection of nanocatalytic materials.

Finally, the ballistic out-of-plane motion of our photocatalytic microswimmers suggests a photoreactor design where the competition between gravity and activity is exploited. Realizing motion control in 3D, by, for example, dynamic light patterning, could induce complex flows, which in turn enhance overall reactor efficiencies in traditionally difficult-to-mix settings. Such control would not only be favorable for mixing in microfluidic channels, which have similar dimen-
sions to the observed Z displacements of the microswimmers, but also in flat-panel reactors where mass transfer is a key limiting factor. Increased reaction rates arising from microswimmer motion have been previously demonstrated, but applicability has been limited by materials and scalability. By targeting societally relevant reactions such as water splitting, we hypothesize that large quantities of microswimmers could be exploited in a novel photoreactor concept where the particles possess a dual catalyst-stirrer functionality. Therefore, incorporating aspects of chemical reaction engineering and soft matter physics could help overcome the four-phase mass-transfer limitations inherent to current photocatalytic systems.

4. Experimental Section

**Nitrodopamine Synthesis:*** Nitrodopamine was synthesized following well-established protocols. Briefly, dopamine (5 g, 32.6 mmol) and sodium nitrite (6.3 g, 91.3 mmol) were dissolved in 150 mL water and cooled to 0°C under stirring in an ice bath. 25 mL sulfuric acid (20 v/v%) was added dropwise and left stirring at RT overnight. The product mixture was cooled once more to 0°C, filtered, and washed with copious amounts of twice-distilled water at 0°C and then ethanol at 0°C. The resulting nitrodopamine hydrogen sulfate was then dried under high vacuum overnight.

**Poly(acrylamide)-g-(1,6-hexanediamine, 3-aminopropyl-dimethyloxy-
silane, nitrodopamine) Synthesis:** Synthesis of the pentafluorophenyl acrylate monomer and its polymerization were performed following previously published protocols. Briefly, pentafluorophenol (87.21 g, 0.47 mol) was dissolved in 150 mL of dichloromethane (DCM) at 0°C and 2,6-dimethylypyridine (0.55 mL, 0.52 mol) was added slowly through a dropping funnel, which was rinsed afterward with another 150 mL of DCM. This second portion was added to the reaction mixture. Acryloy chloride (42.14 mL, 0.52 mol) was then added dropwise to the reactor, still under cooling, and left to react overnight under N$_2$ atmosphere at room temperature. The resulting 2,6-dimethylypyridine hydrochloride salt was removed by filtration and the residual solution was washed three times with 100 mL of water, dried with magnesium sulfate, and the solvent evaporated under reduced pressure. The product monomer was purified by distillation (in two portions) under reduced pressure (10 mbar) to give a colorless liquid (97.09 g, 78%). The monomer pentafluorophenyl acrylate (14.31 g, 60.13 mmol), the initiator AIBN (23.83 mg, 0.15 mmol), and the chain-transfer agent 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (158.45 mg, 0.43 mmol) were dissolved in 15 mL of toluene inside a Schlenk tube. The solution was degassed via three freeze-pump-thaw cycles and left to react under a nitrogen atmosphere at 80°C in an oil bath for 18 h. After the RAFT polymerization was completed, the mixture was left to cool to room temperature and the resulting polymer (pPFPAC) isolated by precipitation in methanol and dried under vacuum for 48 h (12.90 g, 90%).

Likewise, the post-modification steps were carried out as outlined in the work by Serrano et al., with the exception that the (poly) pentafluorocateacet (pPFPAC) backbone was not first PEGylated, and instead was only post-modified with the binding side groups (N-boc-
hexanediame, 3-aminopropyl-dimethyloxyasilane, nitrodopamine). Briefly, N-boc-hexanediame (227 mg, 1.05 mmol) was dissolved in 6.4 mL dimethylformamide (DMF) with an excess of triethylamine (318 mg, 3.15 mmol). The mixture was added drop-wise to pPFPAC (500 mg, 2.1 mmol), dissolved in 5.07 mL DMF, and left stirring overnight at 50°C. A new solution containing 84.5 mmol (0.525 mmol) of 3-aminopropyl-dimethyloxyasilane and triethylamine (160 mg, 1.58 mmol) was dissolved in 7.4 mL of DMF and added drop-wise to the previous solution, still at 50°C, and under stirring overnight. An excess of nitrodopamine was dissolved separately (154.4 mg, 0.525 mmol) in 7.4 mL of DMF with 160 mg of triethylamine (1.58 mmol). The latter solution was added slowly to the polymer solution and left stirring overnight at 50°C. DMF was evaporated under reduced pressure, the mixture re-dissolved in DCM (40 mL, 4 equivalents) and (TFA, 10 mL, 1 equivalent) and left to react under stirring overnight. The resulting mixture was again evaporated under reduced pressure and re-dissolved in twice-distilled water (80 mL). This solution was purified by dialysis against water for two days using a membrane with a MWCO of 3500 Da and subsequently freeze-dried to obtain the yellow-brown poly(acryalamide)-g-(1,6-hexanediame, 3-aminopropyl-
dimethyloxyasilane, nitrodopamine).

**Polymer-Assisted Nanoparticle Attachment onto Microspheres:** Polymer solutions were prepared by dispersing the dry poly(acrylamide)-g-(1,6-
hexanediame, 3-aminopropyl-dimethyloxyasilane, nitrodopamine) in 50°C water overnight under magnetic stirring. The maximum polymer concentration is limited by the solubility of the polymer (approximately 60 mg/L). 1 w/v% SiO$_2$ microparticles suspensions were first added to a bubbling 70°C H$_2$O$_2$/NH$_4$OH solution (1:1 volumetric ratio) under magnetic stirring for 10 min to activate the SiO$_2$ surface with reactive hydroxyl groups. The cleaned particles were then added dropwise under magnetic stirring to the prepared polymer solutions and left stirring overnight (final SiO$_2$ concentration 0.1 w/v%). The polymer-SiO$_2$ particles were then washed by centrifugation to remove excess polymer and redispersed in phosphate-buffered saline (PBS pH 7.0). Nanoparticle suspensions of varying concentrations (PBS pH 7.0 media) were then added dropwise to the...
polymer–SiO₂ suspensions under magnetic stirring and left mixing overnight (final SiO₂ concentration 0.1 w/v%). Finally, the nanoparticle functionalized SiO₂ microparticles were washed extensively with alternating sonication and centrifugation steps to remove any excess nanoparticles not bound to the SiO₂ microparticles.

**Microswimmer Fabrication:** Wax-SiO₂ Pickering emulsions were prepared by adapting the methodology used by Perro et al. Suspensions containing 5 w/v% SiO₂ particles, 10.8 mg/L didodecyldimethylammonium bromide (DDAB), and a 1:10 molten 0.1 M NaCl solution to remove surfactants, before further washing in deionized water. The SiO₂-Wax colloidosomes were dispersed overnight by gentle agitation in an aqueous solution of a post-modified (poly) pentafluorooctacete (pFPFAC) polymer. The pFPFAC-colloidosomes were then washed thoroughly in deionized water before redispersing in a phosphate-buffered saline (PBS) pH 7.0 suspension containing the functional metal-oxide nanoparticles. After gentle mixing overnight, the nanoparticle functionalized colloidosomes were collected by filtration and the wax was finally removed with chloroform.

**Light-Controlled Motion Experiments:** Stock H₂O₂ (30 v/v%, manufacture) was added to dilute particle suspensions of the microswimmers to obtain 300 μL of the desired H₂O₂ concentrations. 280 μL thereof was then pipetted into a flow-through cell (cell 137-QS; Hellma Analytics) with a light path length of 1 mm. Particles were imaged on an inverted microscope under Köhler illumination using a 40× objective (CFI S Plan Fluor ELWD 40X) with adjustable collar (set to 1 mm), and videos were taken at 10 fps on a Hamamatsu C4400-20UP digital camera. UV illumination of the particles (340/380 nm) was achieved using a Lumencor SPECTRA X light engine as the excitation source through the objective.

**Particle Tracking:** Videos were first pre-processed with Fiji (ImageJ) for conversion to 8-bit and cropped to obtain one particle per field of view. Particle centres were tracked using a custom script combining the MATLAB implementation of the Crocker and Grier IDL particle tracking method, and the radial symmetry approach outlined by Parthasarathy. The first invariant moment (inertia) of masks around the particle centres was determined using a MATLAB implementation of Hu’s 7 invariant moments formulation. Inertia look-up-tables (LUTs) were first obtained for stationary and diffusive particles. The evolution of inertia with Z was then inverted, before fitting of a cubic polynomial function with Z was then inverted, before fitting of a cubic polynomial function.

Supporting Information for more details.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Author Contributions**

Author contributions are defined based on the Contributor Roles Taxonomy (CRediT). Conceptualization: M.R.B., F.G., and L.I. Formal analysis: M.R.B. and F.G. Funding acquisition: F.G. and L.I. Investigation: M.R.B. Methodology: M.R.B., F.G., and L.I., and N.S. Software: M.R.B. and F.G. Supervision: F.G. and L.I. Validation: M.R.B. and F.G. Visualization: M.R.B., F.G., and L.I. Writing - original draft: M.R.B., F.G., and L.I. Writing - review and editing: M.R.B., F.G., L.I., and N.S.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

active Brownian motion, active matter, janus, microswimmers, nanotechnology, photocatalysis, scalable

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