Reversed Janus Micro/Nanomotors with Internal Chemical Engine

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Supporting Information

ABSTRACT: Self-motile Janus colloids are important for enabling a wide variety of microtechnology applications as well as for improving our understanding of the mechanisms of motion of artificial micro- and nanoswimmers. We present here micro/nanomotors which possess a reversed Janus structure of an internal catalytic “chemical engine”. The catalytic material (here platinum (Pt)) is embedded within the interior of the mesoporous silica (mSiO2)-based hollow particles and triggers the decomposition of H2O2 when suspended in an aqueous peroxide (H2O2) solution. The pores/gaps at the noncatalytic (Pt) hemisphere allow the exchange of chemical species in solution between the exterior and the interior of the particle. By varying the diameter of the particles, we observed size-dependent motile behavior in the form of enhanced diffusion for 500 nm particles, and self-phoretic motion, toward the nonmetallic part, for 1.5 and 3 μm ones. The direction of motion was rationalized by a theoretical model based on self-phoresis. For the 3 μm particles, a change in the morphology of the porous part is observed, which is accompanied by a change in the mechanism of propulsion via bubble nucleation and ejection as well as a change in the direction of motion.

KEYWORDS: micro/nanomotors, Janus particles, phoretic motion, self-propulsion, mesoporous silica, micromachines

Named after the ancient Roman God Janus, micro- or nanosized particles with an architecture of different physical and/or chemical properties over regions of the surface have been widely explored in various areas of science and technology. Typical Janus “motors” have two distinct faces, at least one of which is “active”, i.e., catalyzes chemical reactions in the surrounding solution, which leads to self-propulsion. Such motile particles are envisioned to enable multiple, break-through applications. For instance, autonomous Janus motors have been used as an active cargo delivery system to transport microparticles12 and small molecules3−6 as well as active micro/nano platforms for environmental applications.7 While there are many methods to fabricate Janus motors,8,9 the most common one is deposition, by sputtering or electron-beam (e-beam) evaporation, of a chemically active material, e.g., Pt, onto a monolayer of spherical particles made of silica, polystyrene, etc.10 The reverse process of covering the surface of a chemically active particle with an inert material11−13 or surface functionalization of chemically active moieties onto one face of an inert Janus particle14,15 has also been employed as methods of fabrication for Janus motors. In addition to the well-known catalytic combination of Pt/H2O2, many other inorganic chemical reactions, such as MnO2/H2O2,16 Al/H2,17 Mg/H2O,18 and Ir/Ni/H219,20 have been utilized in the design of Janus motors. Biocatalytic reactions triggered by enzymes have been explored recently as a means of achieving propulsion of Janus motors.3,6,20

Various mechanisms to convert chemical energy into motility of active colloids have been reported. Bubble propulsion, which can be easily identified by visible gas bubbles detaching from the active side of the motors,11,21−23 is one important mechanism for larger motors, i.e., with characteristic size of...
tens of micrometers. As the motors' size decreases to a few micrometers, bubble propulsion is seldom reported; in this size range, most of the Janus motors exhibit some form—diffusio, electro, electrochemical—of self-phoresis.10,24,25 Although this...
class of mechanisms was intensively studied in the past decade, recent debates in the literature highlight a number of interesting questions on the self-phoretic motion, which are yet to be answered.\textsuperscript{24,26–28} If the size of the active particle is further decreased toward submicrometer scale, any directionality of the motion is lost due to fast rotational diffusion, and the particles exhibit enhanced diffusion.\textsuperscript{4,13,29}

Here, we report on the development of a mSiO\textsubscript{2}-based hollow, spherical Janus motors with “reversed” Janus structure, in that the catalytic layer (Pt) is placed inside the hollow particles, and thus the catalytic reaction takes place only inside the cavity as well, in contrast to conventional Janus motors (see Scheme 1). By using polystyrene (PS) particles of different sizes as starting templates in the fabrication procedure, we successfully control the size of the motors from 500 nm up to 3 μm. We observed size-dependent motility behavior (see Scheme 1): enhanced diffusion for 500 nm particles; directional phoretic motion toward the nonmetallic side for 1.5 and 3 μm particles, which is rationalized via theoretical modeling; and bubble propulsion toward the metallic side for 3 μm particles, for which a change in the morphology of the porous structure of the motor is also noticeable. These Janus motors with catalytic reactions inside the motors’ body have the advantage that the whole external surface is available for functionalization, compared to conventional Janus motors where only half of the external surface is available. Furthermore, being made out of mSiO\textsubscript{2}, the surface can be easily functionalized with various moieties, and therefore they can act as versatile active micro/nanoplatforms in applications such as environmental remediation and active drug delivery. Via theoretical modeling and analysis, we have shown that the directional motion of the reversed motors, in the absence of bubbles, is compatible with a self-phoretic mechanism. These findings contribute to a better understanding of self-phoresis and to the design and fabrication of other new types of chemically powered micro/nanomotors.

Figure 2. Characterization of the structure and of the motion of the reversed Janus micromotors (1.5 μm). (a) Schematic illustration of the motion, assumed to occur by some type of self-phoresis, of the micromotor. (b) SEM of the micromotor and (c) TEM image of the nonmetallic side of the micromotor. (d) Snapshots of a typical trajectory at 10 wt % H\textsubscript{2}O\textsubscript{2}. Inset: the micromotor moves toward the porous part. The red spot is a label automatically assigned by the tracking software. (e) MSD (average) as a function of the time interval (Δt) and (f) the corresponding average velocity of the micromotor at different fuel concentration. The results in (e and f) are calculated as average over 10 independent trajectories at each fuel concentration; error bars show the standard error of the mean.
RESULTS AND DISCUSSION

We start by succinctly describing the fabrication method. Layers of Pt (10–15 nm) and SiO2 (2 nm) are sequentially deposited on a monolayer of (template) PS, spherical particles, yielding typical Janus particles, as depicted in Scheme 1. (SEM images of Janus PS particles of three different sizes after Pt deposition (JPS-Pt) are presented in Figure S1.) Subsequently, the whole surface is encapsulated, using sol-gel chemistry, by a mesoporous silica (mSiO2) shell; a typical outcome is shown in Figure 1a,b. Due to the different surface properties, hydrophilic SiO2 and hydrophobic PS, the mSiO2 shows a different growth morphology on the two sides. The mSiO2 shell coated on the Pt hemisphere (metallic side) has a uniform and smooth surface with a thickness of about 50 nm (inset of Figure 1b). However, the mSiO2 coated on the PS hemisphere (nonmetallic side) has a rough surface consisting of aggregated small mSiO2 particles. In the final step of the fabrication, the PS template is removed by dissolving it in dimethylformamide (DMF). In this way we successfully obtain mSiO2-based reversed Janus motors, in which the Pt hemisphere (black color) is embedded inside the hollow mSiO2 shell (Figure 1c) (Pt is black, on the left). We noticed relatively large pores/gaps, with a diameter of up to 50 nm, at the nonmetallic side (inset of Figure 1c), which would allow relatively unhindered diffusion of molecular species, such as H2O2 and O2, between the solution inside and outside the shell. In contrast to conventional Janus motors, where the Pt is on the outside of the surface, here the H2O2 decomposition takes place inside the hollow cavity, acting as internal “chemical engine” for the motile Janus particles.

The self-propulsion of the nanosized motors (500 nm diameter) was characterized by optical microscopy observation (see Experimental Section in the SI). Automatic tracking and calculation of mean-square-displacement (MSD) at different time intervals (Δt) was accomplished by a self-developed code based on Python (Figure S2). For the small particles, the rotational diffusion coefficient of the symmetry axis of the particle $D_r = r_t^{-1} = k_B T/(8\pi \mu R^3)$, where $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $\mu$ is the viscosity of the solution, and $R$ is the radius of the nanomotors, is large (note the dependence on $1/R^3$); therefore, the nanomotors have a small characteristic reorientation time $r_t = 0.092$ s at 22 °C, the ambient temperature at which the experiments have been carried out. Typical examples of the motion of the nanomotors without (Video S1) and with (Videos S2 and S3) fuel, respectively, are provided in the Supporting Information (SI). Due to the rapid reorientation of the symmetry axis of the motile colloid, the active nanomotors are expected to exhibit enhanced diffusion, but very weak, if any, directional motion. This is indeed what our experiments show, in that the MSD depends linearly on time, and its slope increases with increasing concentration of fuel. The effective diffusion coefficient $D_{eff}$ is extracted from the slope of the linear dependence as MSD = 4$D_{eff}$Δt (assuming the motion to be two-dimensional, corresponding to trajectories in the focal plane under optical observation). The diffusion coefficient in the absence of fuel is 0.69 ± 0.02 µm^2 s^-1; this value is slightly lower than the theoretical expectation of 0.86 µm^2 s^-1 following the Stokes–Einstein equation $D = k_B T/(6\pi \mu R)$. The dependence of $D_{eff}$ on fuel concentration, summarized in Figure 1d, shows an increase from the Brownian diffusion value (0.69 ± 0.02 µm^2 s^-1) in the absence of fuel to 1.10 ± 0.04 µm^2 s^-1 (at 3 wt % H2O2), 1.31 ± 0.05 µm^2 s^-1 (at 5 wt % H2O2), and 1.49 ± 0.05 µm^2 s^-1 (at 10 wt % H2O2), respectively.

Figure 3. Phoretic motion or bubble propulsion for reversed Janus micromotors of large size (3 µm). (a) Low- and (b) high-magnification SEM images of Janus micromotors (3 µm). (c, d) Schematic illustration of the motion mechanism, and snapshots along a typical trajectory, of micromotor (3 µm) undergoing (c) directional phoretic motion at 10 wt % H2O2 (motion toward the nonmetallic side) and (d) bubble propulsion at 10 wt % H2O2 (motion away from the nonmetallic side).

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We now turn to the case of the larger particles of about 1.5 μm diameter. In spite of large pores and gaps at the nonmetallic side (Figure 2b,c), the micromotors maintain an overall spherical shape. Due to their size, these micromotors have a rotational diffusion time of the symmetry axis \( \tau_r = 2.48 \text{ s} \), which is significantly larger than the relaxation time of the chemical composition of the solution around the colloid by diffusion. In this case, directional self-propulsion of the micromotor (1.5 μm) is observed (Figure 2d), and the MSD curves now show the corresponding parabolic shapes at short times (Figure 2e).\textsuperscript{10,29,30} The dependence of the velocity on the fuel concentration shown in Figure 2f further argues for a mechanism of motion involving the catalytic decomposition of H\(_2\)O\(_2\). The velocity \( V \) of the micromotor was calculated directly from the ratio between the length \( L \) of the trajectory during a known time period \( t \) and the time \( t \). Alternatively, the velocity \( V \) can be estimated by fitting the parabolic part of the MSD with \( 4D \Delta t + V^2 \Delta t \).\textsuperscript{10,30} The values thus obtained are similar to the ones directly calculated as above. Snapshots along a typical trajectory are presented in Figure 2d (see also Video S4). As shown in the inset of the first panel, from these optical observations we can identify the direction of the motion to be toward the nonmetallic side. Since typical, compact core SiO\(_2\)/Pt or PS/Pt Janus spherical micromotors (1–2 μm) also move toward the noncatalytic part of the Janus structure, this observation raises the possibility that the catalytic reaction actually occurs at the external surface of the Pt hemisphere, \textit{via} diffusion of the fuel and product species through the very narrow nanochannels of the smooth mSiO\(_2\) shell covering the Pt film (inset of Figure 1b). To test this possibility, we have used motors without removal of the PS core, which thus do not have the “cavity” available for reactions. When such motors are suspended in 5 wt % H\(_2\)O\(_2\) solution, we have not observed either indications of H\(_2\)O\(_2\) catalytic decomposition or motion of the particles (Video S5). Therefore, we rule out this possibility and conclude that the motion is due to chemical reactions occurring inside the cavity of the particle. Further discussion of this case, including a theoretical analysis that provides an explanation for the motility and the direction of motion, is presented below.

By using larger PS particles (about 3 μm) as templates, micromotors with a different morphology of the nonmetallic side are obtained: Instead of a shell with quasi-uniform porosity, now the motor has a shell with one large hole (Figure 3a,b). For this type of micromotor, we observe, at the same fuel concentration (10 wt % H\(_2\)O\(_2\)), either phoretic motion or bubble propulsion; snapshots from typical trajectories are shown in Figures 3c,d (Videos S6 and S7, respectively). The red arrows indicate the location from where the bubbles are released. The coexistence of two mechanisms of motion can be explained by the fact that formation of bubbles depends not only on the O\(_2\) concentration reaching the nucleation threshold but also on the surface morphology, the roughness of the pore orifice at the nonmetallic side, and whether the rest of the shell is porous or not (which influences the probability for nucleation due to significantly changing the interior O\(_2\) concentration that is “funneled” toward the “hole”).

Figure 4. (a) Schematic illustration of the model and notations. (b) Density (scaled by \( C_0 \)) of solute molecules (color coded) inside (left legend) and outside (right legend) the particle. (c) Flow of the solution (streamlines) in the fixed (laboratory) system when the interior and exterior flows are hydrodynamically coupled by transmission of tangential stress; the color codes the magnitude of the flow velocity (scaled by \( V_0 \)) inside (right legend) and outside (left legend) the particle, respectively. (d) The velocity of the particle (scaled by \( V_0 \)) as a function of the ratio \( \beta \), of phoretic mobilities (see the main text) for various values of the porosity parameter \( k \) and slip-lengths (specifying the strength of the interior/exterior hydrodynamic coupling), as given in the main text. (Also see the main text for the definitions of \( C_0 \) and \( V_0 \)).

Figure 1b).
On the other hand, the phoretic mechanism remains operational independently of these factors.

In line with previous reports on bubble propulsion, we have observed that under similar concentrations of fuel the velocity of micromotors moving by bubble propulsion is significantly larger (by a factor of 10 in the current experiments) than in the case of phoretic motion. Motion by bubble propulsion can be promoted by adding a surfactant, e.g., sodium dodecyl sulfate (SDS, 0.5 wt %) to the solution. Upon addition of SDS, we observed very fast velocities of micromotors driven by bubble propulsion (Figure S3 and Video S8), up to about 500 μm s⁻¹; at the same time, the phoretic motion was completely suppressed, an effect previously reported but yet to be conclusively explained. We note that for the smaller micromotors (1.5 μm), where the porous structure of the shell is missing the “funneling” large hole, addition of SDS did not lead to bubble propulsion.

We rationalize the directed motion exhibited in the absence of bubble formation by using a simple model of a chemically active colloid and of motion by self-phoresis. The model bears of bubble formation by using a simple model of a chemically catalyzed reaction. The solute molecules diffuse uniformly across the whole shell, and no external fields acting on the particle or on the fluid; furthermore, in the range of velocities that are observed experimentally and in the absence of bubble formation, the flow of the solution is in the low Reynolds number regime, and the diffusion of the molecular solute is dominant over advection, i.e., the Pécel number of the solute is small.

At steady state, and under the assumption that the rotational diffusion of the particle is slow compared to the relaxation of the distribution of solute by molecular diffusion, the density \( c(r) \) of solute molecules (in the fixed system of coordinates, shown in Figure 4a), which is chosen such that it is centered at the instantaneous position of the center of the particle) is the solution of the Laplace equation \( \nabla^2 c(r) = 0 \) subject to appropriate boundary conditions. These are (i) on the catalyst covered region, the current of solute molecules along the normal (into the particle) direction equals the production by the source: \(-D\partial_n c = Q \); (ii) vanishing current along the direction of the normal into the particle over the smooth silica part; (iii) over the porous part, the outgoing (at the cavity side of the porous shell) solute molecules current equals the one outgoing at the outside of the porous shell; the magnitude of this current at the point \( r_p \) on the porous region is assumed to be proportional to the difference in density across the porous shell, i.e., \( j(r_p) = K[c_o(r_p) - c_o(r)] \), where \( c_o \) denotes the density of solute on the inside and the outside of the particle, respectively. The phenomenological parameter \( K \) (units of velocity) is a measure of the porosity of the shell: for small values of \( K \) the density of solute on the outside of the shell is much smaller than that on the inside, while for large values of \( K \) the two densities are comparable. Physically, \( K \) is bounded by the fact that transport of solute molecules through the porous shell cannot be faster than transport through free solution. For a thin shell with thickness \( \delta \), an upper bound for \( K \) can be estimated as \( K_{\text{max}} = D/\delta \). The diffusion problem outlined above can be solved in the standard way via a series representation of \( c(r) \) in spherical coordinates (see S1). In Figure 4b we show an example of solute density distribution \( c(r) \) in units of \( C_0 \) as an example of solute density distribution \( C_0 := Q R/D \). Since \( Q \) is the dimensionless porosity parameter \( k = K R/D \).

Due to the effective interaction of the solute molecules with the surface of the colloid, the gradients in solute density along the surface of the particle give rise to stresses in the fluid and thus to hydrodynamic flow. Over the nonporous surfaces (the Pt covered one and the compact, smooth silica part), these interactions are accounted for by a so-called “phoretic slip” hydrodynamic boundary condition on the surface of the particle; i.e., \( u_n = -b \nabla c \) at the surface, with the phoretic mobility \( b < 0 \) for repulsive (attractive) interactions, respectively. The parameter \( b \) can take different values over the surface, \( b_{\text{Si}} \) and \( b_{\text{Si}} \) based on previous studies, we expect both of them to be negative and the ratio \( b_{\text{Si}} / b_{\text{Si}} < 1 \).

The role played by the porous part of the surface in the phenomenon of slip leads to the effective hydrodynamic flows inside and outside of the shell. In this case, the model maps directly into self-diffusiophoresis of the whole shell plus the solution contained inside. This is driven by the distribution of solute on the outside of the shell, the phoretic mobility \( b_{\text{Si}} \) on the compact (smooth) silica part, and the boundary condition specifying the tangential component of the flow velocity over the porous part. (The assumption of a hydrodynamically insulated interior implies that the radial component of the flow velocity vanishes at all points on the shell.) For simplicity, we assume that over this porous part, an effective phoretic slip boundary condition, characterized by a mobility \( b_{\text{por}} \) holds; this parameter is expected to satisfy \( b_{\text{por}} < 0 \) and \( |b_{\text{por}}| < |b_{\text{Si}}| \), since the porous matrix is silica. Irrespective of the value of \( b_{\text{por}} \) within those limits, we obtain \( V < 0 \). This is opposite to the direction of motion observed in the experiments, which conclusively argues against this mechanism as a potential explanation of the experimental observation.

We therefore consider in detail a second possibility: While the porous shell prevents a significant radial flow between the inside and the outside, it still allows for transmission of tangential stress from the inside to the outside of the porous shell. This “spilling-into” scenario has been extensively studied in the context of flow over porous walls, and we model it here as an effective hydrodynamic slip boundary condition for the hydrodynamic flow \( v \) over the porous part: \( \nu_{\text{eff}}(r_o) = -\langle \nu \rangle / \mu \sigma_{\text{eff}} \). Here \( \sigma_{\text{eff}} \) denotes the \( \theta \) component of the stress tensor \( \sigma \) of the Newtonian liquid and the minus sign is due to the fact that the normal to the inner surface of the shell is opposite to the unit vector of the radial direction (see S1). Here the slip-length parameters \( \lambda \) have rather the meaning of a “leakage depth” of the flow inside of the cell. In the following, we set them to the values 100 nm (the inside) and 50 nm (outside), since for the mechanism to be operational, the inside value is expected to be larger than the thickness (\( \delta \sim 50 \text{ nm} \) of.
the porous shell, while the outside is expected to be smaller than the inside by about δ. We note that these values are not special, in that we have obtained the same phenomenology described below for a range of values V0/δ ≥ 90 nm. The (i) photoric slip and the hydrodynamic slip boundary conditions, together with (ii) the requirement of vanishing radial flow on the surface of the shell, (iii) the rigid translation of the particle with velocity V, (iv) vanishing flow far away from the particle, (v) incompressibility of the flow, and (vi) force free motion of the particle, completely specify the solution of the Stokes equations (i.e., the flow) and the velocity V of the particle; the details of the calculation are provided in the SI. In Figure 4c we show an example of hydrodynamic flow inside and outside a porous particle which moves with a positive (i.e., toward the nonmetallic side) velocity V/V0 ≈ 0.06 (where V0:= lbb′lC0/(2R)), corresponding to the slip-length values noted above and to b′ = 0.1.

Once the slip-length parameters are fixed, the velocity depends only on the values of k and 0 ≤ b′ ≤ 1. As shown in Figure 4d, while the dependence on k is rather weak (note, though: under the assumption that the solute remains dissolved and no bubbles are formed), the magnitude and, most importantly, the sign of the velocity depend on the value of b′. Previous studies indicate that small (<0.3) values of this ratio are required in order to capture the emergence of wall-bound steady states of motion for compact (i.e., not porous) silica-Pt particles. In that same range of b′ values, our model predicts motion of the porous particle toward the nonmetallic side, which is in agreement with the experimental observations. This feature provides a welcomed self-consistency check of the model.

CONCLUSIONS

In summary, we have fabricated, studied experimentally, and theoretically modeled a spherical micro/nanomotor with reversed Janus structure. This consists of a mesoporous silica spherical external shell and a catalytic Pt hemisphere embedded inside the hollow cavity. The porous structure at the nonmetallic side of the motors provides the means for chemical species exchange with the surrounding solution such that the catalytic decomposition of peroxide inside the particle can power self-propulsion. Motors of different diameters (500 nm, 1.5 μm, and 3 μm) exhibit distinct types of motion: enhanced diffusion, photoric motion, and either bubble propulsion or phoretic motion, respectively. The motion by self-phasoris, as well as its direction, has been rationalized by developing a theoretical model which accounts for the chemical reactions taking place inside the cavity and coupling of the hydrodynamic flows inside and outside the cavity.

In addition to the flexibility in the type of motion, these micro/nanomotors have the whole external surface made of mesoporous silica, and thus they can be readily modified with versatile functional moieties. Such features promote the Janus motors with reversed structure in the position of promising candidates for active micro/nanoplatforms capable of fulfilling on-demand tasks, such as environmental remediation or active drug delivery, in liquid environments.

METHODS

Materials. Tetraethylorthosilicate (TEOS, 99%), triethanolamine (TEOA, 99%), cetyltrimethylammonium bromide (CTAB, 99%), ethanol (>99%), 2-propanol, polyvinylpyrrolidone (K-30, > 99.5%), 2′-azobis(isobutyronitrile) (AIBN, 98%), 2′-azobis(2-methylpro-
Experimental sections about fabrication of the Janus motors with reversed structure, SEM characterization of Janus particles, video recording, MSD analysis, and details of the theoretical modeling. (PDF)

Videos S1–S4 (ZIP)
Videos S5–S8 (ZIP)

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Author Contributions
X.M., S.J., D.-P.K., and S.S. initiated this project. X.M. and S.J. prepared the Janus motors with reversed structure and carried out experiments of SEM imaging, optical video recording, and MSD analysis. A.M.-L. developed the code for MSD analysis. M.N.P. and W.E.U. developed the theoretical modeling. K.H. conducted the TEM imaging. S.S. supervised the project. X.M., M.N.P., W.E.U., and S.S. analyzed the results and wrote the paper.

Notes
The authors declare no competing financial interest.

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