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# **Comparative Studies of Light-Responsive Swimmers: Janus** Nanorods versus Spherical Particles

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ABSTRACT: The shape of objects has a strong influence on their dynamics. Here, we present comparative studies of two different motile objects, spherical Ag/AgCl Janus particles and polystyrene Janus nanorods, that move due to an ionic self-diffusiophoretic propulsion mechanism when exposed to blue light. In this paper, we propose a method to fabricate Janus rodlike particles with high aspect ratios and hemispherical tip shapes. The inherent asymmetry due to the ratio between capped and uncapped parts of the particles as well as the shape anistropy of Janus nanorods enables imaging and quantification of rotational dynamics. The dynamics of microswimmers are compared in terms of velocities and diffusion coefficients. We observe that despite a small amount of the Ag/AgCl reagent on the surface of rodlike objects, these new Janus micromotors reveal high motility in pure water. While the velocities of spherical particles reach 4.2  $\mu$ m/s, the single rodlike swimmers reach 1.1  $\mu$ m/s, and clusters reach 1.6  $\mu$ m/s. The effect of suppressed rotational diffusion is discussed as one of the reasons for the increased velocities. These



Janus micro- and nanomotors hold the promise for application in light-controlled propulsion transport.

# ■ INTRODUCTION

Colloidal particles appear in diverse geometrical shapes, both in nature and commercially manufacturing. On the one hand, there are natural "colloids" represented by biominerals that can be readily organized to give their complex forms and diverse properties.<sup>1-3</sup> On the other hand, the recent advances in chemical synthesis and microfabrication led to "artificial colloids" with properties and shapes that have not been presented until now, for example, tetrapods,<sup>4</sup> shape gradient particles,<sup>5</sup> polymer polygonal and curved structures,<sup>6</sup> and internally structured colloidal particles.<sup>7</sup> Shape, together with other properties, e.g., electric,<sup>8,9</sup> magnetic,<sup>10</sup> other stimuli responsiveness,<sup>11,12</sup> crucially influences the dynamics of such micro- and nanoobjects in a liquid environment. Numerous interesting phenomena related to their orientation arise from the shape of rodlike particles. Among them are nematic ordering of rods in dense solutions,<sup>13</sup> clustering,<sup>14</sup> pattern formation,<sup>15</sup> flocking,<sup>16</sup> and swarming.<sup>17,18</sup>

A basic concept of self-propelled machines involves the use of the nonequilibrium state that produces a dynamic and asymmetric distribution of product particles on the surface and leads to the propulsion of the object. Therefore, particles with shape asymmetry and anisotropic surface properties are possible options for the design. Regardless of the materials and techniques employed, Janus particles are usually fabricated by surface modification or compartmentalization.<sup>19,20</sup> Microand nanodevices converting light energy into kinetic energy act as the so-called light-driven motors.<sup>21-24</sup> The earliest example of an artificial light-powered motor is an azobenzene-based

molecular machine that was reported in the 1980s.<sup>25</sup> A review article by Xu et al.<sup>26</sup> summarizes primary studies and design strategies of light-induced micro/nanomotors as well as some photoactive materials. The design of light-driven Janus motors highly relies on using photoactive materials such as  $\text{TiO}_2$ ,<sup>2727</sup>  $\text{TiO}_2$ -Au,<sup>28,29</sup>  $\text{TiO}_2$ -Pt,<sup>30</sup> Ag,<sup>31</sup> and AgCl.<sup>32,33</sup> The photocatalytic activity of a material is the ability to create electronhole pairs under photoillumination. The most common photocatalysts are semiconductor-based materials with welldefined band gaps, which determine their light-response regions and eventual photocatalytic performance. For Janus particles, the photocatalytic reaction occurs on the cap with the depletion of reactants and the generation of ions, such as H<sup>+</sup> Ag<sup>+</sup>, and Cl<sup>-</sup>. The electrolyte gradients derived from the ionproducing photochemical reaction results in a self-generated electric field around the Janus particle. The micromotors move in response to the generated electric field with a direction dependent on their surface charges.<sup>27,28,34</sup> It is known that Ag/ AgCl has a strong absorption ability and photocatalytic activity in the visible (blue) and near-infrared regions because of the coupling of the surface plasmon resonance effect between AgCl crystals and Ag layers.<sup>35</sup> The asymmetric photodecomposition

diffusion

**Rotational** 

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of AgCl creates a localized electrolyte gradient obtained from the much faster diffusion of H<sup>+</sup> than Cl<sup>-</sup> ions. The concept of enhanced absorption ability in the visible spectral range due to plasmonic photocatalysis was applied in the fabrication of Ag/ AgCl-based spherical Janus micromotors with high motility of up to 800  $\mu$ m<sup>2</sup> within 8 s.<sup>36</sup> The authors demonstrated that polystyrene–silver/silver chloride (PS–Ag/AgCl) micromotors were capable of large-scale displacements in different physiological solutions. However, AgCl exhibits normal diffusion at greater time intervals due to the generation of Ag byproducts, which cover the particle surface and thus impede the ion-producing reaction.

Here, we present the synthesis procedure of monodispersed rodlike polymer particles with tunable dimensions, experimentally investigate the dynamics of Janus nanorods, and compare them to the behavior of the spherical Janus particles in terms of velocities and averaged translational  $(D_t)$  and rotational  $(D_r)$  diffusion coefficients. Three models for the prediction of D<sub>t</sub> and D<sub>r</sub> of nanorods were tested: hydrodynamic stick theory (HS theory),<sup>37</sup> Tirado and Garcia de la Torre's relations (TT theory),<sup>38,39</sup> and Broersma relations (BR).<sup>40,41</sup> HS and TT are appropriate for nanorods of all aspect ratios, while the BR is valid only for cylinders with length-over-width ratios larger than 3.5 in a viscous medium. In our experiment, the aspect ratio of the nanorods is 15. We demonstrate the suitability of TT and BR models for the prediction of Brownian  $D_t$  and  $D_r$  for PS-Ag/AgCl nanorods. We observe strong decoupling between translational and rotational diffusion, which is attributed to the suppressed rotational mobility but promoted translational mobility of Janus particles. The proposed generic approach allows changing parameters to optimize particular features or functions of the nanorods and their clusters.

# EXPERIMENTAL SECTION

Preparation of PS Nanorods with Hemispherical Tips. First, anodic aluminum oxide (AAO) templates were fabricated by two-step anodization,<sup>42,43</sup> as described in the Supporting Information (SI). Next, 50  $\mu$ L of PS/toluene solution (0.2 g/mL) was placed on top of the AAO membranes. Then, the membranes with the polymer solution were left for 4 h at room temperature for slow solvent evaporation. To remove the residual solvent, AAO templates with the PS bulk film were annealed for 18 h at 80 °C. As a next step, the AAO membranes with the PS bulk film were annealed for 6 h under Ar while applying a load of 0.3 bar at 160 °C and then cooled to room temperature at the rate of -5 °C/min for homogeneity and thermal relaxation of the PS film. To induce the wettability transition of PS inside the AAO pores, the AAO templates with the PS bulk film were annealed in a poly(ethylene glycol) 400 (PEG 400) bath at 80 °C for 1 h for PEG infiltration into the pores of AAO. To complete dewetting of the polymer, the AAO templates with the PS bulk film were annealed at 200 °C for approximately 4 h in a PEG 400 bath. Afterward, AAO membranes with embedded nanorods having a hemispherical tip shape were washed with deionized water and ethanol five times and dried at 40 °C for 18 h. The information about the materials and chemicals used in our work is provided in the SI.

**Metal Deposition.** *Microspheres.* Monolayers of 2  $\mu$ m PS particles were prepared by the drop-casting PS-ethanol suspension onto a Si wafer cleaned in piranha, a mixture of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in a ratio of 3:1. Then, the deposition of the 30 nm Ag layer on arrays of PS microspheres was performed.

Nanorods. In turn, the same thickness Ag (30 nm) layer was deposited on top of the hemispherical tips of nanorods immobilized on the AAO template using a physical vapor deposition machine at a base pressure of  $7 \times 10^{-7}$  mbar.

The synthesis of PS–Ag/AgCl was performed using the same protocol for the spherical and rodlike objects. The process is described elsewhere.<sup>33,36,44</sup> To synthesize PS–Ag/AgCl particles, the Janus Ag-coated nanorods were immersed in a mixture of poly(vinyl pyrrolidone) (PVP) and FeCl<sub>3</sub> solutions. Previously, 270 mg of FeCl<sub>3</sub> crystals was dissolved in 50 mL of water at room temperature. Then, 1.665 g of PVP powder was added to the solution. To dissolve the PVP completely, the prepared PVP/FeCl<sub>3</sub> solution was kept in an ultrasonic (US) bath for 5 min. The rodlike Ag/AgCl Janus particles were prepared by placing the Ag nanorods in the PVP/FeCl<sub>3</sub> solution. Finally, the Petri dish was wrapped in aluminum foil and placed onto an orbital shaker for 20–30 min. Then, the solution was centrifuged and the particles were resuspended in deionized (DI) water. To remove PVP and FeCl<sub>3</sub> solutions, the PS–Ag/AgCl particles embedded into the AAO template were washed in DI water, at least, five times.

PS-Ag/AgCl particles were released from the AAO pores using a 5% KOH aqueous solution. Initially, we bend an AAO template to put it in a 2 mL Eppendorf tube. Subsequently, 2 mL of 5% KOH was added. When the side with PS-Ag/AgCl nanorods became shiny, we removed the AAO template from the solution with tweezers. The PS nanorods were centrifuged at 2000 rpm for 2 min and then washed with DI water. The centrifugation and washing steps were repeated at least eight times to ensure the removal of base residue. The samples were washed with DI until reaching a neutral pH of 7. The pH values of solutions were measured using a pH indicator. In turn, spherical particles were detached from the Si wafer by ultrasonication for 15–30 min. The particles were kept suspended in DI water and stored at 4 °C for future use, preferably in a dark Eppendorf tube to protect them from exposure to light.

To achieve the directed motion of PS-Ag/AgCl particles, we used a fluorescent lamp with a Zeiss filter (excitation with BP 450-490 nm and emission with LP 515 nm), which is controlled by opening or closing the shutter. The blue light intensity was  $106 \pm 1 \ \mu\text{W} \text{ mm}^{-2}$ .

**Video Recording and Analysis.** The trajectories of particles were obtained from video-based particle tracking. All videos with a field of view of approximately 70  $\mu$ m × 70  $\mu$ m were captured at a frame rate of 28.57 frames per second (fps). A total of 11 spherical and 10 rodlike separate Janus particles were tracked using a LabView (National Instruments) script providing particle trajectory, orientation, and timing. The average video length was 35 s. Six videos were recorded for single nanorods performing Brownian motion. Captured video duration was 25–50 s for each particle. Three clusters of two nanorods and two clusters of three nanorods were observed over 25–170 s.

**Characterization.** Scanning electron microscopes Zeiss Auriga (Carl Zeiss Microscopy GmbH, Germany) and Raith 150 Two (Raith GmbH, Germany) and optical microscope Olympus BX52 (Olympus Deutschland GmbH, Germany) were used as the two characterization techniques for the investigations. Scanning electron microscopy (SEM) inspection was carried out at an accelerating voltage of 3 kV. To characterize the surface of charged colloids,  $\zeta$ -potential measurements were performed by a Malvern Zetasizer Nano ZSP (Malvern Panalytical Ltd, U.K.). The particles were dispersed in DI water and equilibrated for 1 min at 25 °C prior to investigation. Three tests were performed for each sample.

## RESULTS AND DISCUSSION

**Spherical and Rodlike Janus Particles.** In this work, we compare Janus nanorods and microspheres with the same cap thickness, compounds, and hydrodynamic diameters  $(d_h)$ . For our experimental investigations, the nanorods with a diameter of 400 nm and a length of 6  $\mu$ m and microspheres with a diameter of 2  $\mu$ m were chosen. We selected PS as the organic part of the microswimmers due to their commercial availability with narrow molecular weight distributions over a wide molecular weight range. To choose the appropriate size of particles for the comparison, several important experimental

parameters need to be taken into account. More detailed information on the experimental requirements is provided in the SI. We estimated the hydrodynamic diameters of the nanorod based on the equivalent sphere<sup>45,46</sup> with the translational diffusion coefficient  $D_t = 0.21 \ \mu \text{m}^2/\text{s}$  predicted by the BR model<sup>41,47</sup> using the Stokes–Einstein relation

$$d_{\rm h} = \frac{k_{\rm b}T}{3\pi\eta D_{\rm t}} \tag{1}$$

where  $k_{\rm b}$  is the Boltzmann constant, *T* is the temperature,  $\eta$  is the viscosity of water, and  $D_{\rm t}$  is the translational diffusion coefficient. This results in the same  $d_{\rm h} = 2 \ \mu {\rm m}$  of both objects under investigation: microsphere and the single nanorod.

Suitable AAO templates schematically shown in Figure 1a were prepared for template-based fabrication of rodlike



Figure 1. Fabrication of Janus nanorods (a-d) and Janus microspheres (e-g). PS-Ag/AgCl Janus nanorods with uniform size distribution were produced using the template-based technique. AAO was used as a template. (a) Cross-sectional and top schematic diagrams of the AAO template. (b) Infiltration of the PS melt into the AAO template. The SEM micrographs show the PS nanorods inside the AAO. One side of the rods was connected to an underlying PS film. The length of a single rod was approximately 4  $\mu$ m, and the width is 400 nm. The protrusion of the meniscus inside the pore directs the formation of PS nanorods. The pore diameter was also one parameter affecting the increase of the meniscus. (c) Formation of round tips. Electron micrographs of PS nanorods after heating in PEG: top view of the PS nanorods confined in the AAO template (left) and PS nanorods that were released from the template in 5 wt % KOH (right). The nanorods were 6  $\mu$ m in length and 400 nm in diameter. (d) Deposition of Ag and its conversion into Ag/AgCl. SEM images of PS-Ag/AgCl Janus single nanorods (left) and clusters of two nanorods (right). The grainy morphology of the Ag/AgCl layer is shown in green/yellow. (e) Monolayer of PS microspheres obtained by spin-casting. (f) Ag layer was deposited on PS microspheres via thermal evaporation and then converted into Ag/AgCl. (g) Resulting PS-Ag/AgCl Janus microspheres.

particles. PS nanorods were generated by infiltrating the PS melt into the nanopores under Ar, as illustrated in Figure 1b. The direct infiltration of the polymer into the AAO template resulted in bullet-shaped nanorods with nonsymmetrical tips. Based on previous studies,<sup>48,49</sup> we modified the method to manipulate the tip shape of the PS nanostructures inside the AAO membrane. It is known that the polymer melt is a lowsurface-energy liquid that tends to wet the pore walls.<sup>50</sup> In our experiment, the wettability transition of the PS melt to alumina from wetting to nonwetting was used. The comments on the fabrication process are provided in the SI. Figure 1c demonstrates the array of PS nanorods, which remained inside the AAO nanopores after the separation of the PS film in PEG. The length distribution and the curvature of the PS nanorods were found to be rather homogeneous. The geometrical form of the rods could be described as a particle with the cylindrical middle section and hemisphere on each end. This method allowed controlling dimensions and tip shape of nanorods made from a huge number of polymer and polymer-based composite materials.

Next, we prepared the large area self-assembled monolayer of spherical PS particles, as illustrated in Figure 1e. Then, a thin layer of Ag was evaporated onto an array of 2  $\mu$ m PS microspheres, as shown in Figure 1f. To achieve selfpropulsion of the microscopic objects, the asymmetric release of reaction products on the surface of the particle, which exerts osmotic or interfacial forces and propels the particle in a fixed direction, was necessary.<sup>51</sup>

In this study, both types of Janus particles, rods and spheres, were propelled by the photocatalytic reaction of Ag/AgCl under blue light. Ag/AgCl composites have strong absorption in the visible and near-infrared range.35 To achieve the photocatalytic propulsion of the colloidal particles, the Ag layer was converted into Ag/AgCl following the established procedure.<sup>52</sup> In this case, AgCl particles were formed in the immediate vicinity of the Ag layer. The characteristic size of AgCl nanoparticles is 50–100 nm.<sup>36</sup> Figure 1g summarizes the nanoparticulate morphology of Ag/AgCl caps on PS particles. Asymmetric light-driven photocatalytic PS-Ag/AgCl Janus nanorods with an aspect ratio of 15 were obtained by coating one tip of the nanorod with a 30 nm layer of Ag followed by conversion of Ag into Ag/AgCl, as depicted in Figure 1d. Some particles aggregated during the release of PS-Ag/AgCl Janus nanorods from the AAO template. In this case, the nanorods were able to overcome the electrostatic barrier and fall into the van der Waals attraction, which dominates at small separations. The particles stood together by van der Waals forces and were inseparable by mechanical efforts for particles with dimensions below 2  $\mu$ m. Motions of single nanorods, clusters of two and three Janus nanorods (cluster 2 and cluster 3, correspondingly), and spherical particles were investigated in a frame of this study as separate micro- and nanomotors. The snapshots of particles are depicted in Figure 2a-f.

Light-Driven Motion of the Janus Rods and Spheres. As a preliminary step to experimental investigation, we have



Figure 2. Snapshots of active Janus nanorod in different time points oscillating in focus and out of focus (a-c): reorientation from the parallel to perpendicular state. Snapshots of cluster 2 (d), cluster 3 (e) and spherical particle (f). The scale bar is 5  $\mu$ m.

measured the  $\zeta$ -potentials of PS-Ag/AgCl Janus particles in pure water. For spherical Janus micromotors, the  $\zeta$ -potential was  $-15.1 \pm 3.6$  mV (three measurements) at room temperature, T = 25 °C. In turn, the  $\zeta$ -potential was -22.4 ± 4.3 mV (three measurements) for the Ag/AgCl Janus nanorods. For comparison, the  $\zeta$ -potential measured in the solution of noncoated PS nanorods was  $-31.6 \pm 4.4 \text{ mV}$ (three measurements). Hence, the Janus particles in contact with the aqueous solution were negatively charged. To isolate the particle dispersion from the environment, a 1 mm thick ring-shaped polydimethylsiloxane (PDMS) spacer was placed onto a precleaned glass slide to contain the solution. Then, a droplet of about 5–10  $\mu$ L of particle suspension was added. Due to the density mismatch and the electrostatic repulsion, the particles settled within a few nanometers on top of the glass surface. To determine the time of sedimentation, we initially focused on large clusters of the Janus nanorods lying on the glass surface and measured the time until almost all nanorods were in the same focal plane with the clusters. The sedimentation time of the particles was measured to be in the range of 30 min due to the small size of the particle and low molecular weight of polystyrene. We observed that the rodshaped Janus nanomotors were located close to the glass substrate and performed three-dimensional (3D) motion going in and out of the focal plane, as shown in Figure 2a-c. The spherical micromotors also were also set in 3D motion. The low intensity of visible light had no observable effect on freshly prepared samples.

To propel the particles in pure water, the chemically asymmetric Janus particles convert the energy provided by light into the kinetic energy by ion-producing reactions. When irradiated with blue light in an aqueous environment, AgCl decomposed as follows<sup>26,53,54</sup>

$$4AgCl + 2H_2O \rightarrow 4Ag + 4H^+ + 4Cl^- + O_2$$

The light-induced decomposition of AgCl to Ag and Cl produces H<sup>+</sup> and Cl<sup>-</sup> ions as reaction products.<sup>33</sup> The resulting distribution of product ions around the micromotor is asymmetric, leading to the phoretic motion of the particle. The authors showed that a dielectric AgCl Janus micromotor clearly moves away from the AgCl side when exposed to UV or strong visible light. Figure 3a depicts the snapshots and the trajectories of PS-Ag/AgCl Janus microspheres. The trajectories of spherical micromotors showed a directed motion. Unlike many reported micromotors that more or less maintain a constant speed over time, PS-Ag/AgCl micromotors slowed down within ~25 s in a gradual and regular way until Brownian motion took over due to backdeposition of the reduced Ag on the surface of the cap. At longer times, the motion of PS-Ag/ AgCl spherical particles reverted to a random walk, in which runs of the directed motion were interrupted by random changes of the direction.

To quantify the above observation, we calculated MSD as a function of time from the tracking data. The MSD was calculated for each individual track based on the method described by Weimann et al.,<sup>55</sup> where MSD for a given time lag  $n\Delta t$  is described as the average over all points for coordinates r = [x(i), y(i)]



**Figure 3.** Motion of PS–Ag/AgCl Janus particles under blue light illumination. (a) 35 s experimental trajectories of single PS–Ag/AgCl spherical Janus micromotors with a time step of 1/28.5 s. The change of the particle position in time is labeled with a rainbow color scale. (b) Gray lines showing the mean-square displacement (MSD) curves of single Janus microspheres and the red MSD curve obtained by averaging over 11 trajectories. (c) Representative trajectories of nanorods and clusters of three nanorods (cluster 3) were taken over 170 s. (d) Average MSD curves of Brownian motion of single nanorods, PS–Ag/AgCl Janus nanorods, and clusters calculated from 5 to 11 videos.

$$\langle r^{2} \rangle = \langle |r(t_{0} + \Delta t) - r(t_{0})|^{2} \rangle$$
  
=  $\frac{1}{l-n} \sum_{i=1}^{l-n} [x(i+n) - x(i)]^{2} + [(y(i+n) - y(i)]^{2}$   
(2)

with *l* denoting the number of frames and  $\Delta t$  denoting the time steps between frames.

Figure 3b shows the MSD curves for 11 single PS–Ag/AgCl microspheres and the MSD curve (red) averaged over these curves. To determine the efficiency of propulsion of spherical micromotors, we calculated  $D_t$  and velocities from the MSD curve following the fitting methodology proposed by Howse et al.<sup>56</sup> The MSD graph has a parabolic form. If we consider a long time of observation ( $\Delta t \gg \tau_r$ ), where  $\tau_r$  is the rotation diffusion time, the MSD is a straight line graph with contribution from the velocity term

$$\langle r^2 \rangle = (4D_{\rm t} + v^2 \tau_{\rm r}) \Delta t \tag{3}$$

where  $\Delta t$  is the time interval and v is the velocity. For a propulsive microswimmer at a short time scale  $\Delta t \ll \tau_r$ , the MSD is given by

$$\langle r^2 \rangle = 4D_t \Delta t + v^2 \Delta t^2 \tag{4}$$

For intermediate times, where  $\Delta t \rightarrow \tau_r$  the transition from ballistic to enhanced diffusion occurs. The velocities of the Janus particles and the translational diffusion coefficients are listed in Table 1.

For PS-Ag/AgCl spherical particles illuminated with blue light,  $D_t$  was found to be 1.68  $\pm$  0.9  $\mu$ m<sup>2</sup>/s. The diffusion coefficient related to the Brownian particle with a radius of 1  $\mu$ m was theoretically estimated to be 0.2146  $\mu$ m<sup>2</sup>/s.<sup>57</sup> The

#### Table 1. Comparison between Theory and Experiments<sup>a</sup>

theory	$D_v (\mu m^2/s)$	$D_{\rm r'}$ (rad <sup>2</sup> /s)	<i>v</i> , (μm/s)
microsphere	0.2146	0.16	0.86
HS	0.1896	0.014	0.76
ΤT	0.2181	0.037	0.87
BR	0.2146	0.035	0.86
experiment	$D_v (\mu m^2/s)$	$D_{\rm r'}  ({\rm rad}^2/{\rm s})$	<i>ν</i> , (μm/s)
microsphere	$1.68 \pm 0.9$	$0.152 \pm 0.035$	$4.2 \pm 1.5$
nanorod (B)	$0.21 \pm 0.05$	$0.036 \pm 0.018$	$0.7 \pm 0.1$
nanorod	$0.29 \pm 0.07$	$0.011 \pm 0.008$	$1.1 \pm 0.3$
cluster	$0.35 \pm 0.1$	$0.003 \pm 0.001$	$1.6 \pm 0.3$

<sup>*a*</sup>Theoretical translational and rotational diffusion coefficients predicted by the hydrodynamic stick model (HS), Tirado and Garcia de la Torre's theory (TT), and Broersma relations (BR) for a single nanorod of 400 nm diameter and 6  $\mu$ m length. Abbreviation B denotes from Brownian motion.

diffusion coefficient for Janus micromotors is 8 times higher than that for Brownian particles. The average velocity of the Janus microsphere  $v = 4.2 \pm 1.5 \ \mu m/s$  was determined from the fit to eq 4.

Figure 3c shows the two-dimensional (2D) position of the center of mass for PS-Ag/AgCl nanorods and a cluster of three nanorods as a function of time. To track the center of a nanorod, we circumscribed the particle by a circle that passed through both tips and had a diameter corresponding to the length of the particle. The radius of the circumscribed circle was changing with time, corresponding to the projection of the length of the particle during three-dimensional motion. The spatial orientation of the nanorod was defined as the angle between the long axis of the nanorod and the horizontal *x*-axis. From the coordinates of the particle trajectory, we calculated the average values of MSD (Figure 3d) and mean-squared angular displacement (MSAD) (Figure 4b) as a function of time. For the calculation of MSD and MSAD, the measurements were sorted in the following way. We excluded all points at which the nanorod was standing perpendicular to the glass substrate, as shown in Figure 2c, corresponding to an apparent length of the nanorod of exactly 1 pixel. The standing up behavior of the nanorods was observed for both Brownian and active rods. Nevertheless, the passive nanorods were found to be more often in the standing state as compared to the active particles. The nanorods remained in the standing states for milliseconds to seconds. The weight of the particle determines whether it sediments at the bottom of the device or spends significant time in the bulk. As mentioned in the Spherical and

Rodlike Janus Particles section, the sedimentation rate of rodlike particles was observed to be very low due to the low density of PS (1002 kg/m<sup>3</sup>). The deposition of the tiny amount of Ag/AgCl onto one hemispherical tip of the nanorods did not change substantially the sedimentation rate. The weight of the particle competes against the Brownian motion, which promotes diffusion into the bulk. We assume that the active caps prefer to be on top of the rods, upon standing up. The motion of rods is constricted by a glass slide from one side (bottom), while the other direction (top) remains unlimited. For active spherical PS-Ag/AgCl particles, the motion is triggered toward the noncapped PS face. Let us assume that active nanorods also move toward the noncapped PS part. Then, if the cap of the rod is faced toward the glass slide, the reaction on the cap will promote escape from the bottom surface to the unlimited bulk (lying position). When the swimming velocity of the particle is oriented toward the particle gravity, the nonsymmetrical distribution of the reaction products will push the rod to diffuse very close to the bottom surface, promoting the standing behavior.

The particle tracking algorithm mistakenly detects changes in the orientation of the nanorods, which are larger than  $\pi$ . In these cases, we corrected the values by replacing them by  $2\pi - \Delta \theta_i$ , where  $\Delta \theta$  is a difference between *i* and *i* + 1 angular positions of the nanorod separated by time  $\Delta t$  within a trajectory.

Figure 3d indicates the change of MSD with time under exposure to continuous illumination with blue light (blue and green curves) and for the purely Brownian motion (red curve). For the Brownian motion, the squared displacement is linear in time, while PS-Ag/AgCl rodlike particles under blue light illumination demonstrates different diffusive behaviors depending on the time scale of observation. The observed movement could be expressed in terms of rotational and translational diffusion coefficients. The translation diffusion coefficient associated with the Brownian motion was determined experimentally to be 0.21  $\pm$  0.05  $\mu$ m<sup>2</sup>/s in pure water. At the same time, the diffusion coefficient related to PS-Ag/AgCl nanorods was found to be 0.29  $\pm$  0.07  $\mu$ m<sup>2</sup>/s, slightly higher than that for the Brownian motion. The photocatalytic reaction has a pointlike nature that generates torque rather than pure translational motion. Using these MSD plots, we also calculated the propulsive velocities. The velocity of a single Brownian nanorod was  $0.7 \pm 0.1 \ \mu m/s$ . On a short time scale, Janus rod-shaped particles exhibited a superdiffusive motion with a velocity of  $1.1 \pm 0.3 \ \mu m/s$ .



Figure 4. Angular orientation of rodlike particles with respect to the x-axis as a function of time (a). The rotation of Janus particles is suppressed as compared to the rotation of the Brownian motion. (b) Mean-squared angular displacement (MSAD) of the nanorods and microspheres as a function of lag time, nanorods of 6  $\mu$ m length, and clusters of two nanorods and three nanorods. For comparison, the average MSAD curve of Brownian motion of single nanorods is shown in red.



Figure 5. Fluctuations of the apparent length of Janus particles around the actual length of the nanorods over time (a). Accuracy of the angular detection depends on the apparent length of the PS-Ag/AgCl nanorods (b). Here, individual pixels are represented by squares. The 2D projections of particles are shown as blue pixels. The increasing length results in more information and precise and reliable angular position detection.

The motion of a composite depends significantly on the number of particles involved. We found several active clusters consisting of two and three rods. We admit the lower statistical output for the cluster data, as such assemblies with the same mutual localization of the rods resulting in similar shapes and dimensions can be rarely found in the suspension. Since two MSD curves obtained for cluster 2 and cluster 3 were not significantly different, we combined the data on cluster 2 and cluster 3 and considered them as a single system. The difference between the single active nanorods and cluster systems was observed to be statistically significant. Figure 3c shows the representative trajectories of a cluster and two single nanorods over 165 s on the glass surface. As seen in the figure, the motion of the cluster is approximately straight. This indicates that the suppression of the rotational motion was more pronounced compared to the single nanorod. The more reactive the Ag/AgCl materials, the faster the clusters propelled and the greater the distances they cover. The MSD of clusters showed a parabolic dependence on time for all measured time scales (Figure 3d). The diffusion coefficients  $D_{t}$ from the MSD curves were calculated as  $0.35 \pm 0.1 \ \mu m^2/s$ . The effect of the increasing Ag/AgCl surface area on the rate of a reaction could be estimated from the comparison of velocities of individual particles with the velocities of welldefined clusters comprising two and three PS-Ag/AgCl nanorods. The velocity of the cluster was 1.6  $\pm$  0.3  $\mu$ m/s. The photocatalytic reaction on Janus clusters was more intensive as compared to the reaction on single particles.

Figure 4a represents the time-dependent change of the orientation of single Janus nanorods before and after irradiation with blue light. The orientation of a Brownian particle underwent a random rotation, while the active Janus particle exhibited a directed motion. These directed motions could be described as fluctuations around zero. The amplitudes of fluctuation were in the order of 2 rad for single Ag/AgCl Janus nanorods, 1 rad for cluster 2, and approximately 1.5 rad for cluster 3.

The magnitude of rotation can be described in terms of the rotational diffusion coefficient  $D_r$ . The rotation diffusion was investigated by calculating the MSAD, defined as<sup>58</sup>

$$\langle \theta^2 \rangle = \langle |\theta(t_0 + \Delta t) - \theta(t_0)|^2 \rangle \tag{5}$$

where  $t_0$  is the time at the first moment of observation.  $D_r$  can be extracted from the linear fit of the MSAD curve

$$D_{\rm r} = \frac{\langle \theta^2 \rangle}{2\Delta t} \tag{6}$$

We fitted the MSAD data to eq 6 to obtain  $D_r$ . The linear fits of the experimental MSAD curves are shown in Figure 4b in gray. The method proposed by Charsooghi et al. was also used to calculate  $D_r$  for active rodlike particles.<sup>59</sup> For the PS–Ag/ AgCl spherical Janus particle, the  $D_r$  amounted to approximately 0.152  $\pm$  0.035 rad<sup>2</sup>/s. In comparison, the  $D_r$  of the pure PS particle with a diameter of 2  $\mu$ m was estimated to be 0.16 rad<sup>2</sup>/s. The experimental  $D_r$  for PS–Ag/AgCl nanomotors during exposure to blue light was 0.011  $\pm$  0.008 rad<sup>2</sup>/s, while  $D_r$  associated with the Brownian motion was 0.036  $\pm$ 0.018 rad<sup>2</sup>/s. Thus, the  $D_r$  for the Brownian particle was 3.3 times higher than that for the blue-light-driven nanomotor. Clusters demonstrated higher resistance to rotation as compared to single nanorods. The average value of  $D_r$  for the cluster was calculated as 0.003  $\pm$  0.001 rad<sup>2</sup>/s.

We compared the theoretical predictions based on  $TT^{38,39}$ and  $BR^{40}$  and the measured values of translational and rotational diffusion coefficients for rodlike particles. All experimental results and theoretical estimations for  $D_t$  and  $D_r$  are summarized in Table 1. The experimentally observed values  $D_t$  and  $D_r$  for nanorods performing normal Brownian motion are in reasonable agreement with TT and BR. The rotational diffusion of the active spherical particle was suppressed by the reaction on the cap as compared to the theoretical value for the Brownian motion.

Above, we discussed the changes in swimming behaviour by examining the angular position of particles. Figure 5a reveals the changes in the apparent length of a Janus nanorod performing the Brownian motion (red curve), a Janus nanorod (blue curve), and a cluster of three particles (green curve) when illuminated with blue light. Here, the apparent length of the microswimmer corresponds to the projection of the particle on the two-dimensional (x-y) plane. Random fluctuations of the length of the nanorods in the range from 2.0 to 6.2  $\mu$ m were detected for Brownian particles. The length of the cluster varied from 2.8 to 6.2  $\mu$ m within 100 s. Single Janus particles oscillate in a broad range from 0.15 to 8  $\mu$ m due to the photocatalytic reaction on their surface. Lengths beyond 6  $\mu$ m indicated that the particles left the focal plane. The fluctuations of the apparent length of the rodlike particles are crucial for the estimation of the diffusion of Janus particles. Figure 5b illustrates the experimental accuracy in the definition of the orientational position depending on the length of the nanorod. As a first example, we consider the nanorod having a length of two pixels (~0.3  $\mu$ m). Let us fix one side of the nanorod at the center of the 2D coordinate system. As a next step, we assume that the angular orientation of the particle was

changed from 0 to 70°. Due to the pixel spatial resolution, the program for particle tracking will be only able to detect angular changes with a step size of  $\pm 45^{\circ}$ , as shown in the figure. Hence, the detected angle is 90°. In this case, the uncertainty in the measurement of the angular position arises due to the small length of the nanorod. The longer the particle, the more precise the measurement of its angular positions. For a particle projection of 6  $\mu$ m, the measurement uncertainty is less than 2°. The uncertainty in the detection of the angular position of the Janus nanorod as a result of radius oscillation may cause difficulties in comparison of the degree of rotation changes. Real 2D tracking leads to shorter and less precise tracks that are contained in the focal plane.

The experimental results on the tracking of the position of the particle revealed that the rotational diffusion of Janus nanorods was suppressed when they were driven into motion. Hence, the rotational diffusion coefficient scales down as  $R^{-3}$ with increasing apparent radius R of an active particle. Here, the apparent radius reflects the actual size of the particle observed under the microscope, taking into account its location with respect to the focal plane. Another reason is that the rotation of Janus clusters may be also suppressed by the chemical reaction. It was shown that the enhanced concentration gradient of products near the contact point of Pt caps of clusters consisting of two spherical PS-Pt Janus micromotors led to the suppression of rotational diffusion in H<sub>2</sub>O<sub>2</sub>.<sup>60</sup> In our experiment, asymmetric active Janus particles were rigidly "glued" along the long axis due to van der Waals interaction forming a cluster. The concentration distribution of the photocatalytic reaction products formed around and in between the caps of two Janus nanorods could have also promoted the directional translational motion.

The reasons for the decrease of the rotation diffusion coefficient for clusters may be the following. The Ag/AgCl surface quickly darkens upon exposure to blue light by disintegrating into elemental chlorine and metallic silver in an aqueous solution. Since the entire reaction takes place on the surface, the amount of the surface area of the Ag/AgCl cap on the particle surface determines the propulsive effectiveness of the swimmers. We estimated the surface areas occupied by Ag/ AgCl caps for microspheres with a radius of 1  $\mu$ m, nanorods, and a cluster of two nanorods. The estimation was based on the SEM images of Janus motors. We calculated the ratio between the reactive cap surfaces and the nonreactive PS parts. For PS-Ag/AgCl microspheres, the ratio was estimated to be 0.5 (half of the particles are coated with Ag/AgCl). For nanorods, only one half-spherical tip with a diameter of 0.4  $\mu$ m was coated with Ag/AgCl. The total surface of the nanorod can be represented by the side of the cylinder, which when unrolled is a rectangle with sides of 6 and 1.256  $\mu$ m, and the surface of the sphere with a radius of 0.2  $\mu$ m. The ratio of the active part of the rodlike swimmer to the total surface area is 0.03. This means that the reaction took place only on 3% of the surface of the nanorod and the amount of reactant was enough to propel the particle. The active surface area of the cluster doubled as compared to that of a single particle. At the same time, the nonreactive surface area increase was 1.7 times higher compared to that of a single nanorod. The ratio between reactive and nonreactive surface areas was approximately 0.04, 25% higher than that of a single particle. Indeed, this hypothesis needs to be additionally verified with more observation of clusters consisting of different numbers of nanorods.

Due to the effect of suppression of rotational diffusion and the interplay of electric fields generated on the Ag/AgCl caps, the cluster system was able to reach velocities up to 1.5 times higher than that of the single nanorod. Despite a relatively large amount of Ag/AgCl on the surface, the spherical Janus particles showed velocities less than 2.5 times higher than the velocity of the cluster. The reason could be the difference in the distribution of electric and flow fields around the moving spherical and rodlike Janus particles caused by the shapes and sizes of Ag/AgCl caps. When the particle is irradiated with UV light, only a thin layer of AgCl participates in the reaction. Simulations performed by Zhou et al. for spherical PMMA-AgCl Janus particles showed that due to the near-field slip flow from the uncoated to the coated half the moving direction is away from the AgCl cap.<sup>33</sup> In our experiments, all spherical PS-Ag/AgCl Janus micromotors moved away from the caps. In the case of rodlike particles, due to the poor optical contrast between the nanorod and cap and the out-of-focus position, it was impossible to follow the Ag/AgCl cap. Therefore, it is hard to conclude in which direction did the rodlike Janus particles and clusters move. The fluctuation of nanorods around certain orientations indicates that the elongated shape influences the distribution of ionic and fluid flows around the rodlike Janus particles.

# CONCLUSIONS

To summarize, we synthesized single PS-Ag/AgCl active Janus nanorods and their clusters that, when illuminated with blue light, are capable of measurable propulsion. To determine the coordinates of rodlike particles and their angular positions, we developed an algorithm for the recognition and 3D tracking of particles relying on their projections. The algorithm allowed us to sort the measurements excluding points at which the particles were standing perpendicular to the glass substrate. Despite the tiny amount of the active photocatalytic material, the asymmetric rodlike PS-Ag/AgCl nanomotors were capable of displacements. For such chemically active systems, directed motion at short time scales has been successfully achieved. Large clusters consisting of two and three Janus nanorods showed more ability to self-propel due to the same orientation of individual particles in the cluster. For comparison, the spherical PS-Ag/AgCl Janus micromotors having the same cap thickness, keeping the same chemical compositions and hydrodynamic diameters as the nanorods were also prepared. We investigated experimentally the motion of different micro- and nanomotors and compared their propulsion efficiency in terms of velocities and translational and rotational diffusivities. The comparison between the velocities of the single Janus nanorods and Janus clusters demonstrates that the velocity of the cluster was up to 1.5 times higher than that for the nanorods. The velocity of the spherical Janus particle was only 2.5 times higher than the velocity of the cluster. By defining reorientational mean-square angular displacement rodlike particles, a caging behavior of the rotational motion of nanorods can be recognized. The rodlike Janus particles with controllable aspect ratios and tip shapes can be used to create a whole new class of light-powered nanomotors.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.0c01913.

Movies S1-S6 and additional information about sample preparation and analysis (text S7) (PDF)

Movies showing the blue light-induced and Brownian motion of micro- and nanomotors (avi) (ZIP)

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#### Notes

The authors declare no competing financial interest.

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