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Organized Self-Assembly of Janus Micromotors with Hydrophobic Hemispheres

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S *Supporting Information*

ABSTRACT: Organized self-assemblies of Janus catalytic motors, induced by hydrophobic surface interactions involving multiple motor/motor and motor/nonmotor particles, display controlled coordinated self-propulsion. The influence of the self-assembled structures upon the motion behavior is investigated. A dynamic 'on-the-fly' assembly is observed during the continuous movement of the individual components, along with changes in the motion behavior. Organized assemblies of multiple motor/nonmotor particles are also illustrated toward optimal cargo transport and delivery. Such controlled structures and motion of chemically powered Janus micromotor assemblies hold considerable promise for the creation of intelligent nanomachines that perform collective tasks.

Locomotion of synthetic nano-/microscale objects through fluid environments is one of the most exciting and challenging areas of nanotechnology.[1−10] Self-propelled nano-/microscale machines have demonstrated considerable potential for performing diverse operations and important tasks, including isolation of biomaterials,[11,12] nanotool-based drilling,[13,14] cell manipulation,[15,16] delivery of therapeutic payloads,[17,18] and environmental remediation.[19] Particular recent attention has been given to chemically powered catalytic nanowires,[2−4] tubular microengines,[20−22] and Janus micromotors[23−27] that exhibit autonomous self-propulsion in the presence of hydrogen peroxide fuel. Janus particles, named after the Roman god Janus, are nano-/microscale particles with two distinct surfaces each exhibiting differing physical properties.[28−31] Catalytic Janus particles which are half-coated with a Pt layer move autonomously in a hydrogen peroxide fuel solution in response to gradients of oxygen formed by decomposition of the fuel.[23−25]

Inspired by animal interactions, the ability of synthetic microscale motors to produce self-organized structures is of considerable interest, owing to their future implications in nanomedicine, nanomachinery, transport systems, and chemical sensing.[32−34] For example, translating microscale movement to the macroscopic level would require cooperative action of multiple micromotors. Such coordinated action holds particular promise toward multiple-motor driven transport of large cargo. While many aspects of such coordinated movement of animals are still not fully understood, they have inspired substantial research efforts toward the self-organization of synthetic nanomaterials. Mallouk and Sen studied the schooling behavior of light-powered AgCl micromotors in water due to the diffusiophoresis mechanism.[35] Howse's team reported that doublets of catalytic Janus particles can rotate with different orientations,[36] while Sanchez et al. described the transport of cargo by pairs of Janus micromotors.[27] However, such interactions between catalytic motors have been induced by random aggregation and not by controlled directed assembly and specific attachments. To our knowledge, there are no reports on the controlled guided formation, organization, and motion of dynamic assemblies of multiple Janus particle motors based on specific and directional interactions. Recent reports from Granick et al. described methods for the directed self-assembly of nonmotor Janus microparticles involving hydrophobic poles (hemispeheres).[37−41] Various distinct assembly patterns, in which each Janus sphere was coordinated with other neighbors through hydrophobic interactions, were demonstrated,[37−41] but not in connection to motion.

Here we introduce the first example of spatially guided organization of chemically powered Janus motors induced by hydrophobic surface interactions involving multiple motor/motor and motor/nonmotor interactions. We demonstrate the controlled propulsion of such highly ordered micromotor assemblies and that the self-assembly process can occur dynamically during the movement. The influence of the self-assembled structures upon the coordinated movement of multiple Janus motors is investigated. The self-organization of motor microparticles with opposite hydrophobic and catalytic faces leads to controlled high-order motor assemblies where the hydrophobic sides of neighboring particles face each other (Figure 1), in a manner analogous to the orientation-dependent particle organization described by Granick's team.[38] In addition to the directed organization of multiple motors, we will illustrate the dynamic assembly of multiple motors and multiple-cargo particles using mixtures of catalytic and noncatalytic microparticles toward organized cargo loading and delivery.

In this paper, the Janus motors consist of hydrophobic octadecyltrichlorosilane-modified silica microspheres that are capped with a catalytic Pt hemisphere patch. As illustrated in Figure 1A, neighboring motors thus experience attractive hydrophobic interactions between their exposed OTS-modified silica hemispheres, leading to defined spatial assemblies. The catalytic Pt patch restricts the interparticle attraction to the hydrophobic hemisphere while maintaining a wide range of orientational freedom for each motor in the assembly.

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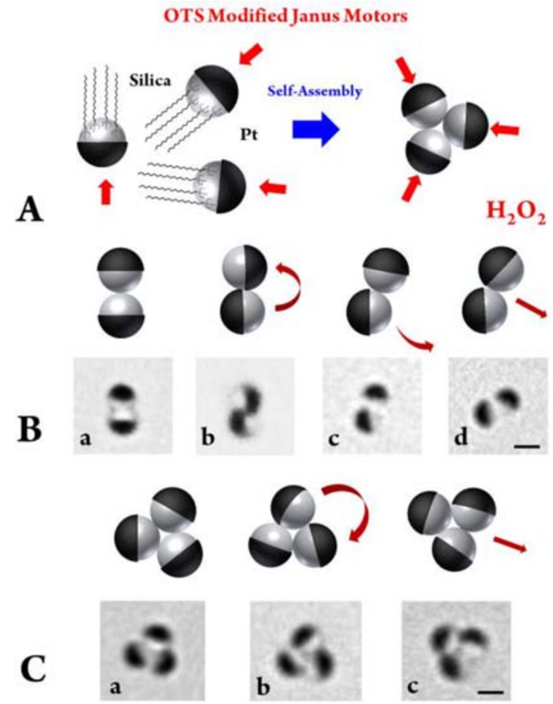

Figure 1. (A) Schematic of the assembly of OTS modified Janus micromotors, with the hydrophobic OTS sides facing one another. (B) Typical doublet Janus motor assemblies: (a−c) movement of Janus motor doublet assemblies with different orientations (taken from SI Video 1). (C) Typical assemblies of Janus motor triplet assemblies: (a−c) movement of triple-motor assemblies with different orientations (taken from SI Video 1). Scale bar, 1 μm. Conditions, 5% hydrogen peroxide.

The asymmetric distribution of the catalyst on the surface of such assemblies thus imparts a net force and net torque to the system. As expected, different bonding orientations between these hydrophobic Janus motors induce different forms of motion. The relative orientation of each motor in the assembly changes its contribution to the net propulsion force and rotational moment. Figure 1 (and SI Video 1) illustrates different movement behaviors of doublet (B) and triplet (C) motor−motor assemblies with various bonding orientations. Figure 1B(a) shows that the symmetric bonding of two such motors results in a nondirectional Brownian motion due to the opposing symmetric forces. In contrast, translational and rotational motion can be observed for motors with angled bonding orientations (Figure 1B(b−d)). In Figure 1B(b), representing an extreme case of minimal contact, the opposite-facing motor doublet displays a very fast, stationary rotation corresponding to a very high angular velocity (of over 30 rad/s) and near-zero rotational radius. The intermediate-angled motor doublet, shown in Figure 1B(c), displays a slow angular velocity (2.5 rad/s) with a larger rotational radius (11 μm). The angled bilaterally symmetric dual motor of Figure 1B(d) displays a nearly linear motion, with a very large rotational radius and near-zero angular velocity (the rotational radius and angular velocity would be ideally infinite and zero in this case). These microscope images clearly indicate that the interactions between the individual motors of the doublets occur between their hydrophobic hemispheres, reflecting the controlled assemblies of the Janus micromotors. As indicated from the corresponding videos, these motor doublets retain their distinct motion pattern. Previous randomly formed doublets[36] have been connected also through their catalytic patches. Similar movement characteristics are observed in Figure 1C for organized triplet motor assemblies. For example, Figure 1C(a) demonstrates that a highly symmetric assembly of three motors, formed by hydrophobic interactions, leads to a nondirectional Brownian motion with no net translational movement. In contrast, a rotational symmetric assembly of the three motors, with an offset angle (Figure 1C(b)), results in fast spinning motion about the centroid (13.5 rad/s). Figure 1C(c) illustrates a triplet assembled with bilateral symmetry that moves in a directional linear path. Any orientational deviation of a single motor will change the moment of the assembly as a whole and affect the translational and angular velocity of the assembly, as illustrated in the doublets of Figure 1B(c) and 1B(d).

The hydrophobic interactions between individual micromotors and micromotor assemblies can promote a continuous growth of the assembly during its movement and lead to dynamic changes in the motion behavior. For example, Figure 2 and the corresponding SI Video 3 illustrate an 'on-the-fly' doublet-to-triplet switching due to the self-attachment of a moving single Janus motor. Prior to this capture, the doublet travels in a circular path with a large radius. However, the resulting symmetric triplet assembly rotates (spins) rapidly around its centroid (with a minimal radius). These data clearly illustrate that the self-assembly mechanism can occur dynamically during the continuous movement of motors and their assemblies.

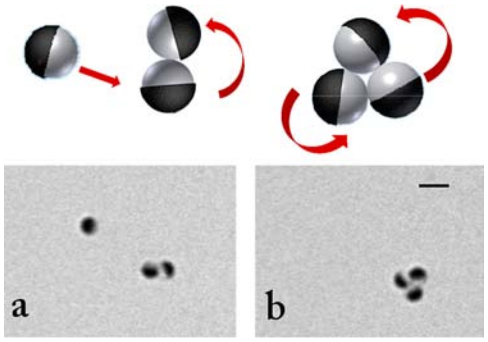

Figure 2. Janus motor assembly: dynamic 'switch' from doublet to triplet configurations (taken from SI Video 2). Scale bar, 2 μm. Conditions: same as those in Figure 1.

SI Figure 1 and SI Video 3 compare the behavior of Janus micromotors with (A) and without (B) the hydrophobic coating. As expected, the control experiment without such a hydrophobic coating shows multiple randomly moving unassembled single Janus motors (B). Such a lack of assembly for the uncoated microparticles can be attributed to the electrostatic repulsion between the charged surface regions.[37] In contrast, the hydrophobic hemispheres lead to the formation of multimotor assemblies (A). Simultaneous dynamic movement of different single, doublet, and triplet motor assemblies can thus be observed over a small area. Overall, these data clearly illustrate that hydrophobic forces are crucial for the formation of distinct assembly patterns and further support their role in the motor organization process.

In addition to the doublet and triplet assemblies, multiple Janus motors can form additional structural patterns. For example, four motors can self-assemble into a 3-D tetrahedral structure (SI Figure 2 and SI Video 4). Due to the symmetric contributions of the driving force from each motor, such a quartet displays only Brownian motion. It is possible to control the specific orientation and cluster shape of the assembled Janus particles by controlling the colloidal valence through optimization of the hydrophobic surface area.[39,40] For example, particles with different half opening angles will form different cluster shapes.[40] Smaller hydrophobic patches can restrict the motor assembly to clusters of up to four particles.[37] However, increasing the patch size would allow the growth of larger assemblies.

In addition to assemblies of multiple Janus micromotors, the new concept allows a directed assembly of motors/nonmotors using noncatalytic hydrophobic microparticles acting as cargo. Such capability for organized loading of multiple cargo particles onto a single motor or assembly of multiple motors holds considerable promise for tailor-made cargo pickup toward optimal active transport and delivery. The Janus motor/nonmotor particles assemble into configurations that maximize the hydrophobic interactions with each other to form structures that minimize the potential energy.[41] Figure 3a (from SI Video 5) demonstrates the formation and movement of a doublet consisting of a single Janus particle motor with a single nonmotor particle. As expected, the doublet moves in a direction perpendicular to the hemispherical boundary. Figure 3b demonstrates a triplet assembly with dual motors and a single nonmotor which again demonstrates a nearly translational motion. The structure of Figure 3c (formed from three motors and one nonmotor particle) differs slightly from the ideal tetrahedral assembly for a quadruplet. This planar quadruplet assembly species commonly exists since deviations from the ideal configurations are possible as a result of the larger valence of the hydrophobic hemisphere and the spontaneous deformation of structures from the relatively weak attractive forces and Brownian motion.[41] To obtain ideal multiple motor/single nonmotor assemblies that travel linearly, it is necessary to control the bonding orientation of the motors to the bare cargo particle. This can be achieved by tailoring the size of the hydrophobic patch.[41] Owing to the dynamic nature of the self-organization process, the relative population of each assembly depends on the incubation time. During the experimental time scale used in this study (up to 10 min) the relative frequency of the observed assembly follows the doublet > triplet > quadruplet trend. The resulting doublet, triplet, and quadruplet motor/single nonmotor assemblies display speeds of 12, 4, and 4 μm/s, respectively ($n = 5$), reflecting the trade-off between increased propulsion force and larger fluid drag. The speed of such assemblies remains stable in a dilute particle solution containing a given fuel level.

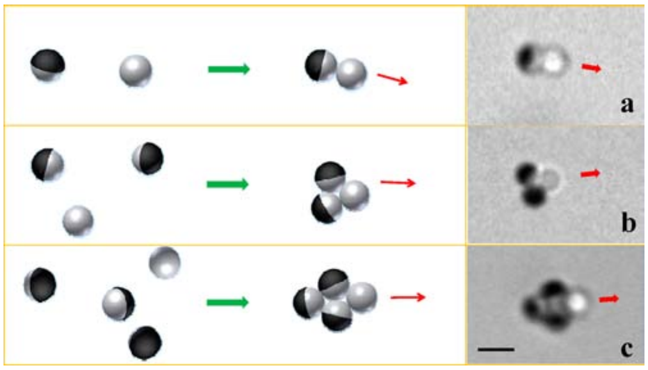

Figure 3. Assemblies of Janus motor/nonmotor microparticles. (Left) Schematic and (right) microscopic images (taken from SI Video 5, right) of (a) doublet, (b) triplet, and (c) quadruplet motor/nonmotor assemblies. Scale bar, 2 μm. Conditions: same as those in Figure 1.

SI Figure 3 and SI Video 6 illustrate a triplet of micromotors (shown in Figure 1C(c)) capturing 'on-the-fly' a single nonmotor particle. The hydrophobic interaction between the motor triplet and the nonmotor particle can be clearly seen from the dynamic uptake of the nonmotor. The resulting assembly has a lower angular velocity and rotational radius as a result of the hydrophobic attachment of the nonmotor particle. The motor/nonmotor interactions allow a continuous pickup of additional cargo while maintaining a well-organized cargo loading process.

Figure 4 illustrates a single Janus motor carrying multiple nonmotor particles (3 in (a) and 6 in (b)) to form organized motor/cargo assemblies through hydrophobic interactions. The single Janus motor is usually self-propelled at a fast speed of 15 μm/s in a 5% w/v hydrogen peroxide solution, corresponding to 12.5 body lengths/s. The speed decreases to 6 and 3 μm/s upon assembling with 3 and 6 nonmotor particles, respectively, reflecting the increased fluid drag force associated with the larger assembly. Such dynamic cargo pickup can continue until the movement stops. A well-defined loading and organization of multiple cargoes on a single motor, in a packed 'flower' type arrangement, can be clearly observed in Figure 4b. Compared to previously reported randomly formed motor/cargo systems[25,27] the new directed assembly method leads to defined motor/multicargo assemblies that minimize the potential energy to offer optimal cargo transport for diverse applications such as targeted drug delivery. Additionally, multiple motor/multiple nonmotor assemblies were also observed in our experiments. For example, SI Figure 4 illustrates an assembly consisting of 2 motors and 2 nonmotors. No obvious net propulsion is observed due to the bilateral symmetry of the opposite catalytic Pt hemispheres and the absence of net force.

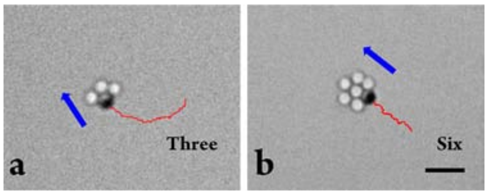

Figure 4. Organized cargo loading. Time-lapse images (over 2 s) of the track lines of motor/nonmotor assemblies: transport of 3 (a) and 6 (b) nonmotor spheres (taken from SI Video 7). Scale bar, 5 μm. Conditions: same as those in Figure 1.

An interesting phenomenon has been observed with some triplet assemblies consisting of a motor doublet and a single nonmotor. As illustrated in SI Figure 5 (and corresponding SI Video 8), such motor/nonmotor triplet assemblies can rotate around the nonmotor particle which serves as the fixed axis of rotation. The hydrophobic interactions between the three particles allow them to remain bonded together, while other interactions between the nonmotor particle and the glass-slide surface (e.g., electrostatic, H-bonding, and van der Waals interactions) allow the assembly to be anchored to the glass surface to form the fixed-point rotation.[42] The direction of rotation is determined by the orientation of the doublet motor assembly. Note, in this case, that the nonmotor particle is also rotating with the motors, but without a net displacement.

In summary, we have demonstrated that hydrophobic interactions provide a new approach for constructing defined assemblies of chemically powered Janus particle motors. These assemblies were prepared by octadecyltrichlorosilane (OTS) modification of the surface of a silica microparticle and addition of a catalytic Pt hemispheric coating. This represents the first example of preparing defined assemblies of micromotors based on specific and directional interactions. The assembly structure along with the individual particle orientations has a profound influence on the movement of such defined micromotor assemblies. Extended higher-order structures are expected by tuning the size and position of the hydrophobic patch beyond the traditional two-faced Janus particle geometry of uniform particle and patch size. A theoretical model will be developed to predict the dynamics of such self-propelled particle assemblies. This attractive assembly strategy allows the cooperative action and coordinated movement of multiple Janus motors, making it promising for diverse future applications ranging from advanced transport to targeted drug delivery. In addition, probing the limits of such autonomous motor assembly systems could help to understand the behavior of biological systems involving multiple moving and interacting components such as fish schooling.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Janus motors preparation and modification protocols, instrumentation, reagents, additional figures, and videos. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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