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## Cooperative transport by flocking phototactic micromotors†

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Cargo delivery by micro/nanomotors provides enormous opportunities for micromanipulation, environmental cleaning, drug delivery, etc. However, due to the limited driving force, it is usually difficult for single micro/nanomotors to transport cargoes much larger or heavier than themselves. Here, we demonstrate that flocking phototactic TiO<sub>2</sub> micromotors can cooperatively transport multiple and different types of large cargoes based on light-responsive diffusiophoresis. Utilizing spontaneous diffusiophoretic attraction, flocking TiO<sub>2</sub> micromotors can load large cargoes. Under UV light navigation, flocking TiO<sub>2</sub> micromotors cooperatively carry and transport cargoes *via* collective diffusiophoretic repulsion in open space or complex microenvironments. After reaching the destination, the carried cargoes can also be unloaded from the flock and be deployed at a predetermined destination by disassembling or reversing the flock. This study may pave the way for developing intelligent swarming micro/nanorobots for cooperative targeting micromanipulation and advancing their applications in drug delivery and microengineering.

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## Introduction

Controllable capture and transport cargoes such as drug molecules, proteins, capsules, and cells in microenvironments is a pivotal nanotechnology that is extensively studied.<sup>1–6</sup> Synthetic micro/nanomotors can extract various energies from the surrounding environment, and convert them into mechanical output allowing for autonomous motions.<sup>7–15</sup> Thus, micro/nanomotors are endowed with the undeniable capability to serve as micro/nanocarriers to realize micromanipulation by establishing physical/chemical interactions between the motors and cargoes.<sup>16–18</sup> Up to now, cargo delivery *via* single micro/nanomotors has been investigated extensively by introducing diffusiophoretic, electrostatic, and magnetic motor–cargo interactions through chemical-powering<sup>19–21</sup> and external-field-driven strategies.<sup>22–27</sup> However, the magnitude of the generated driving forces of single motors would be seriously hindered by their dimensions, thus larger or heavier cargoes are difficult to transport. Inspired by the ant army carrying food cooperatively, the driving force would be much enhanced by grouping the motors.<sup>28–32</sup> Therefore, growing endeavors have been made to construct intelligent micro/nanorobot swarms to cooperatively

transport large cargoes.<sup>33</sup> The key to achieving cooperative transport is to align the forces of active individuals in swarms in the same direction. For example, reconfigurable magnetic motor swarms can regulate their forces effectively in elaborated magnetic fields, thereby manipulating passive cargoes by utilizing hydrodynamic flow.<sup>34,35</sup> Chemically/photochemically powered micro/nanomotors can respond to signaling chemicals secreted by their neighbors and behave as motor groups utilizing local diffusiophoretic interactions.<sup>36–42</sup> Nevertheless, aligning the forces of these individuals to effectively manipulate multiple and different types of large cargoes is still an insurmountable challenge.

In this study, we demonstrate the cooperative transport of multiple and different types of large cargoes by TiO<sub>2</sub> micromotor flocks (TiO<sub>2</sub>-MFs) under UV navigation. Specifically, isotropic TiO<sub>2</sub> micromotors with rich hydroxyl groups can autonomously form clusters based on electrolyte diffusiophoretic attraction, which is also capable of capturing heterogeneous passive large cargoes. Meanwhile, the non-electrolyte diffusiophoretic repulsive force resulting from the photo-degrading H<sub>2</sub>O<sub>2</sub> by the flocking TiO<sub>2</sub> motors can be aligned toward a determined direction against the UV light. Thus, TiO<sub>2</sub>-MFs, even loaded with multiple cargoes, can exhibit negative phototaxis with intense collective expansion. Even though TiO<sub>2</sub>-MFs slow down gradually with increasing loads of cargoes, they can transport up to nine large cargoes. In addition, the carried cargoes can also be unloaded from the flock and be deployed at a designated destination by disassembling the flock into highly dispersed micromotors under intense long-time UV irradiation

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or by reversing the flock away from cargoes. TiO<sub>2</sub>-MFs show broad applicability and excellent feasibility for loading and ferrying different types of large cargoes (SiO<sub>2</sub> microspheres, amino-polystyrene microspheres, carboxyl-polystyrene microspheres and perfluorooctane droplets) benefitting from the universal light-switchable motor-cargo interactions (difusiophoretic attraction and repulsion). The cooperative transport of large cargoes by TiO<sub>2</sub>-MFs in microchannels has also been investigated, manifesting the possibility of realizing cargo transport in microenvironments with complex landscapes. The as-proposed cooperative transport strategy may open a window for the development of general transport systems based on swarming micro/nanorobots to deliver different functional micro/nanoobjects, such as drug capsules, micro-droplets, micromachinery parts for drug delivery, micromanipulation, and microengineering.

## Experimental section

### Materials

Silica, carboxyl-polystyrene, and amino-polystyrene microparticles, as large cargoes, were purchased from Sigma-Aldrich (Shanghai, China), and perfluorooctane was purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Tetrabutyl titanate (TBT) was purchased from Sinopharm Chemical Reagent (Shanghai, China).

### Synthesis of TiO<sub>2</sub> micromotors

The constituent isotropic TiO<sub>2</sub> micromotors used in this work were prepared following previous reports.<sup>26,43</sup> Typically, 25 mL ethanol was mixed with 100  $\mu$ L sodium chloride aqueous solution (0.1 M) and 425  $\mu$ L TBT at ambient temperature. After magnetic stirring for 18 min, the solution was allowed to stand for 24 h. The resulting precipitate was separated, washed three

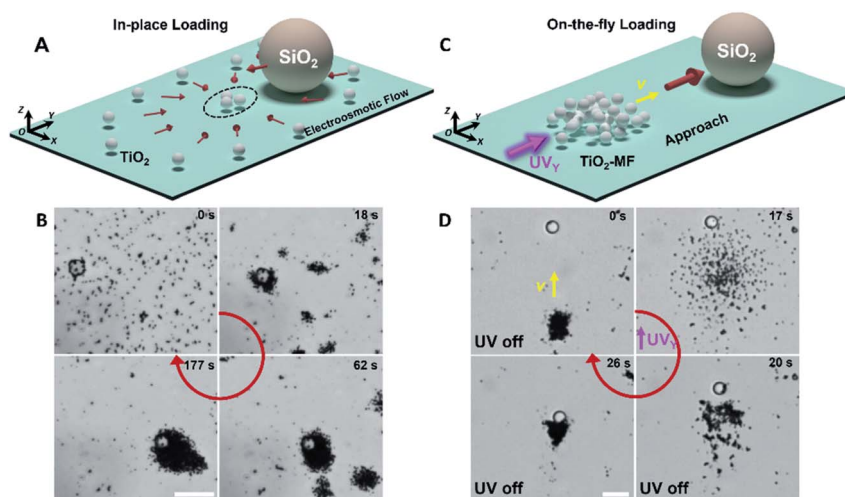
times with alcohol and deionized water, and then dried at 60 °C for 12 h to obtain amorphous TiO<sub>2</sub> microspheres. Finally, anatase TiO<sub>2</sub> micromotors were obtained *via* calcinating amorphous TiO<sub>2</sub> at 300 °C for 2 h.

### Cooperative transport

A 50  $\mu$ L suspension of the TiO<sub>2</sub> micromotors (1 mg mL<sup>-1</sup>) was dropped onto a glass slide (Citotest 1A5107), followed by adding 50  $\mu$ L H<sub>2</sub>O<sub>2</sub> fuel solution (0.75 wt%) and 50  $\mu$ L cargo microparticle suspension (0.03 mg mL<sup>-1</sup>). The dispersed TiO<sub>2</sub> micromotors usually spontaneously gather with the cargo microparticles and form into clusters within five minutes. Four UV-LED light sources (SZ Lamplic Technology, China) with a wavelength of 365 nm and adjustable intensity (0–500 mW cm<sup>-2</sup>) were set above the glass substrate with an incident angle of 45°, as demonstrated in the experimental setup in Fig. S2.† The on/off and incident direction of the UV light were adjusted to investigate the phototaxis of TiO<sub>2</sub>-MFs and their capability for cooperatively transporting large cargoes. The experimental results were observed and recorded at room temperature using an inverted optical microscope (Leica DMI 3000 M, Germany). Videos were analyzed by using ImageJ and Video Spot Tracker V08.01 software. The velocity of the flocks was determined by calculating the displacement of centroid of flocks per second under light irradiation. Over four TiO<sub>2</sub>-MFs were analyzed to obtain the statistic result. The error bar given in the plot is the standard error of the mean.

### Numerical simulation

Numerical simulations were performed using the diffusion module of COMSOL Multiphysics software. The simulation model was built up by immersing a 10  $\mu$ m SiO<sub>2</sub> microsphere surrounded by 65 TiO<sub>2</sub> micromotors (1.2  $\mu$ m in diameter (*d*)) in



**Fig. 1** Two modes of large-cargo loading by TiO<sub>2</sub>-MFs. (A and B) The schematic diagram (A) and optical microscope snapshots (B) depicting the in-place large-cargo loading utilizing spontaneous swarming of TiO<sub>2</sub> micromotors (*d*: 1.2  $\mu$ m) together with a large SiO<sub>2</sub> microsphere (*d*: 10  $\mu$ m). (C and D) The schematic diagram (C) and optical microscope snapshots (D) depicting the on-the-fly large-cargo loading by steering a TiO<sub>2</sub>-MF to approach a large SiO<sub>2</sub> microsphere (10  $\mu$ m). The yellow arrow indicates the motion direction of the flock. H<sub>2</sub>O<sub>2</sub> concentration: 0.25 wt%. Scale bars in (B) and (D): 20  $\mu$ m.



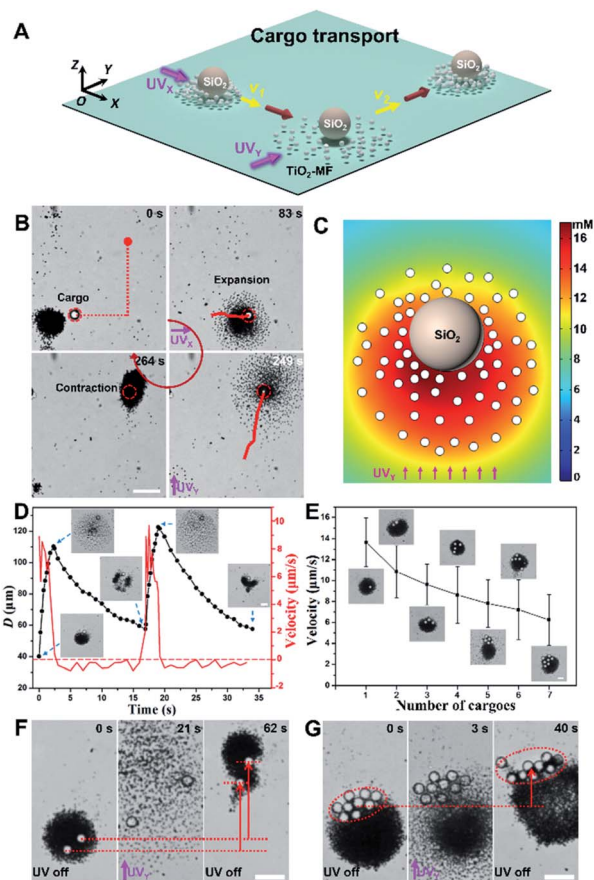
the bottom of a  $0.01 \text{ mm}^2$  square space which was filled with  $\text{H}_2\text{O}_2$  aqueous solution (0.25 wt%). The flux ( $J_{\text{O}_2}$ ) of oxygen molecules from the UV illuminated surface of the  $\text{TiO}_2$  micromotors was set as  $4.13 \times 10^{-4} \text{ mol m}^{-2} \text{ s}^{-1}$  according to the previous report.<sup>43</sup> The diffusion coefficient of  $\text{O}_2$  molecules in water was set to be  $1.97 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ . The distribution of  $\text{O}_2$  concentration was simulated at the steady state, and the average interparticle distance ( $L$ ) was derived from the experimental results of the collective expansion of  $\text{TiO}_2$ -MFs under UV irradiation.

## Results and discussion

The constituent isotropic  $\text{TiO}_2$  micromotors ( $1.2 \mu\text{m}$  in  $d$ ) of  $\text{TiO}_2$ -MFs were fabricated referring to the previous work.<sup>26</sup> According to the reported mechanism, the  $\text{TiO}_2$  micromotors with rich hydroxyl groups secrete  $\text{H}^+$  and  $\text{OH}^-$  ions in aqueous media, and thus can spontaneously gather into clusters due to the diffusiphoretic motor-motor attraction without external energy input.<sup>43</sup> It is noted that this diffusiphoretic attraction can also compel adjacent passive particles to assemble with the  $\text{TiO}_2$  micromotors. Fig. 1A shows the schematic diagram depicting the spontaneous in-place loading of a large  $\text{SiO}_2$  microsphere ( $10 \mu\text{m}$ ) during the gathering of the dispersed  $\text{TiO}_2$  micromotors. As shown in the corresponding experimental microscope snapshots in Fig. 1B, the  $\text{TiO}_2$  micromotors aggregate gradually to form small clusters, and then these small clusters further merge into large clusters along with time progression (ESI Video 1†). Remarkably, multiple large  $\text{SiO}_2$  microspheres could be loaded by the swarming  $\text{TiO}_2$  micromotors (Fig. S1†).

Like other photochemical  $\text{TiO}_2$ -based micromotors, the gathered  $\text{TiO}_2$  micromotors can be powered by photocatalytically decomposing surrounding  $\text{H}_2\text{O}_2$  fuels.<sup>44–50</sup> Under sidewise UV irradiation, the gathered  $\text{TiO}_2$  micromotors exhibit negative phototaxis as a flock ( $\text{TiO}_2$ -MF) in the medium with the  $\text{H}_2\text{O}_2$  fuel,<sup>43,44</sup> and thus can also be driven to approach and load a large cargo on the fly. The on-the-fly cargo loading is illustrated in Fig. 1C and D (taken from ESI Video 2†) shows the corresponding experimental results. Under the navigation of sidewise UV light ( $\text{UV}_Y$  in Fig. 1D), the  $\text{TiO}_2$ -MF moved toward a  $\text{SiO}_2$  microsphere utilizing its dilatational negative phototaxis based on the dominant nonelectrolyte diffusiphoresis (0–17 s in Fig. 1D), and finally loaded it into the flock *via* the electrolyte diffusiphoretic attraction after removing the  $\text{UV}_Y$  (20–26 s in Fig. 1D).

After being loaded by a  $\text{TiO}_2$ -MF, the large cargo can then be transported because it also feels the electrolyte/nonelectrolyte gradients generated by active  $\text{TiO}_2$  micromotors, suggesting that it will move and gather with the flocking  $\text{TiO}_2$  micromotors (in resemblance to a failed constituent in the flock) when the UV light is on and off, respectively. In other words, the active transport of passive cargoes can be achieved by operating  $\text{TiO}_2$ -MFs *via* UV light. Fig. 2A and B depict the schematic diagram and experimental snapshots of the cooperative transport of a large  $\text{SiO}_2$  microsphere ( $d$ :  $10 \mu\text{m}$ ) by a  $\text{TiO}_2$ -MF along the pre-designed path (red dashed lines in Fig. 2B) to a predetermined destination (ESI Video 3†). In detail, when turning on the  $\text{UV}_X$



**Fig. 2** Cooperative large-cargo transport by flocking phototactic  $\text{TiO}_2$  micromotors. (A) Schematic diagram of light-controlled directional cooperative transport of large cargoes by operating the  $\text{TiO}_2$ -MF. (B) A  $\text{SiO}_2$  microparticle ( $d$ :  $10 \mu\text{m}$ ) was delivered by a  $\text{TiO}_2$ -MF along a pre-designed path under the navigation of pulsed UV irradiation. Images are taken from ESI Video 3.† Scale bar:  $10 \mu\text{m}$ . (C) Simulated  $\text{O}_2$  concentration around a passive  $\text{SiO}_2$  microsphere surrounded by 65  $\text{TiO}_2$  micromotors in  $\text{H}_2\text{O}_2$  aqueous solution (0.25 wt%) under UV irradiation ( $500 \text{ mW cm}^{-2}$ ). The interparticle distance was derived from the experimental results on transport. (D) The size ( $D$ ) variation of a typical flock and the velocity variation of the loaded  $\text{SiO}_2$  microsphere versus time under the pulsed UV irradiation. The insets depict the states of the flock and the cargo at various moments. Scale bar:  $10 \mu\text{m}$ . (E) Average motion velocity of typical  $\text{TiO}_2$ -MFs (with similar  $D$ ) carrying different numbers of cargoes ( $\text{SiO}_2$  microspheres with a  $d$  of  $10 \mu\text{m}$ ) under UV light illumination. The insets illustrate the microscopic images of typical flocks loading with different numbers of large cargoes. The error bar of each data point given in the plot is the standard error of the mean of over four different  $\text{TiO}_2$ -MFs. Scale bar:  $10 \mu\text{m}$ . (F and G) The optical microscope snapshots of cooperative transport of two (F) and nine (G) large  $\text{SiO}_2$  microspheres by  $\text{TiO}_2$ -MFs with UV manipulation. Images are taken from ESI Video 4.† Scale bar:  $20 \mu\text{m}$ . UV light intensity:  $500 \text{ mW cm}^{-2}$ .  $\text{H}_2\text{O}_2$  concentration: 0.25 wt%.

(UV light is toward the  $+X$  axis direction), the large  $\text{SiO}_2$  microsphere was pushed expansively *via* nonelectrolyte diffusiphoretic repulsion of the  $\text{TiO}_2$ -MF. Once removing the light, the cargo was dragged back to form a resting flock with  $\text{TiO}_2$  micromotors again at a new central point and showed a net phototactic displacement. When the  $\text{UV}_Y$  (UV light is toward the



+Y axis direction) was then turned on, the flock exhibited an immediate turning toward the +Y direction. The O<sub>2</sub> distribution around a large SiO<sub>2</sub> microsphere surrounded by 65 TiO<sub>2</sub> micromotors in the transport process was simulated by using the diffusion module of COMSOL Multiphysics software. As illustrated in Fig. 2C, upon UV<sub>γ</sub> irradiation, a distinct O<sub>2</sub> concentration gradient forms across the large cargo which can lead to the non-electrolyte diffusiophoresis to propel the cargo. Fig. 2D shows the diameter (*D*) variation of a typical TiO<sub>2</sub>-MF and the velocity variation of the loaded cargo (the large SiO<sub>2</sub> microsphere) *versus* time under two pulsed UV<sub>γ</sub> irradiation, where the instantaneous velocity vector subtly reflects the corresponding pushing and dragging processes discussed above. The cargo moved forward (positive velocity of red curve in Fig. 2D) with the expanding TiO<sub>2</sub>-MF (insets and black curve in Fig. 2D) under UV illumination, and then slightly moved backward (negative velocity of the red curve in Fig. 2D) when the TiO<sub>2</sub>-MF contracted back to a tight resting flock in the absence of UV light (insets and black curve in Fig. 2D). The agreement of these two curves in time proves the synchronized motions of the TiO<sub>2</sub>-MF and the cargo.

More interestingly, the TiO<sub>2</sub>-MF can also transport multiple large cargoes due to its strong driving force (Fig. 2E). Insets in Fig. 2E are the microscope snapshots showing TiO<sub>2</sub>-MFs with similar *D* (*ca.* 50 μm) loaded with different numbers of large cargoes (SiO<sub>2</sub> microspheres). Under the same light and fuel conditions, these TiO<sub>2</sub>-MFs moved slower when carrying more SiO<sub>2</sub> microspheres. Specifically, the average motion velocity of TiO<sub>2</sub>-MFs decreased from 13.7 to 6.2 μm s<sup>-1</sup> when the number of the carried SiO<sub>2</sub> microspheres increased from one to seven. The decreasing velocity can be rationalized by the greater

burden if more passive cargoes were carried while the powering parts (TiO<sub>2</sub> micromotors) were unchanged. The slight difference in the size of TiO<sub>2</sub>-MFs was believed to have a negligible influence on the velocity of these flocks as they had a similar velocity (Fig. S3†). The light-controlled cooperative transport of multiple large cargoes by TiO<sub>2</sub>-MFs is further visually illustrated in Fig. 2F and G (taken from ESI Video 4†), and the displacements in the +Y direction were clearly observed whether the transported cargo number was two or nine (red arrows in Fig. 2E and F).

Besides, TiO<sub>2</sub>-MFs can cooperatively transport different types of heavy cargoes, such as amino- and carboxyl-polystyrene microspheres, and perfluorooctane droplets (Fig. 3). Similar to the spontaneous loading process of the large SiO<sub>2</sub> microsphere (Fig. 1A and B), three different types of large cargoes, including an amino-polystyrene microsphere (*d*: 10 μm), a carboxyl-polystyrene microsphere (*d*: 10 μm) and perfluorooctane droplets (average *d*: 5 μm) can be loaded into the TiO<sub>2</sub>-MF because of the electrolyte diffusiophoretic attraction, and then exhibited synchronized negative phototaxis with TiO<sub>2</sub>-MFs under pulsed UV<sub>γ</sub> light (ESI Video 5†). Fig. 3A, C and E depict the schematic diagrams of transporting corresponding cargoes. The red dashed circles in Fig. 3B, D and F indicate the real-time positions of the cargo particles. These results prove the good adaptability of TiO<sub>2</sub>-MFs, which guarantees the ability to be used in different application scenarios.

Once arriving at a pre-designed destination, large cargoes can be unloaded from TiO<sub>2</sub>-MFs by modulating UV light. Two modes of cargo unloading can be realized depending on the different relative positions of the cargoes and TiO<sub>2</sub>-MFs, including disassembling and reversing the flock, as shown in

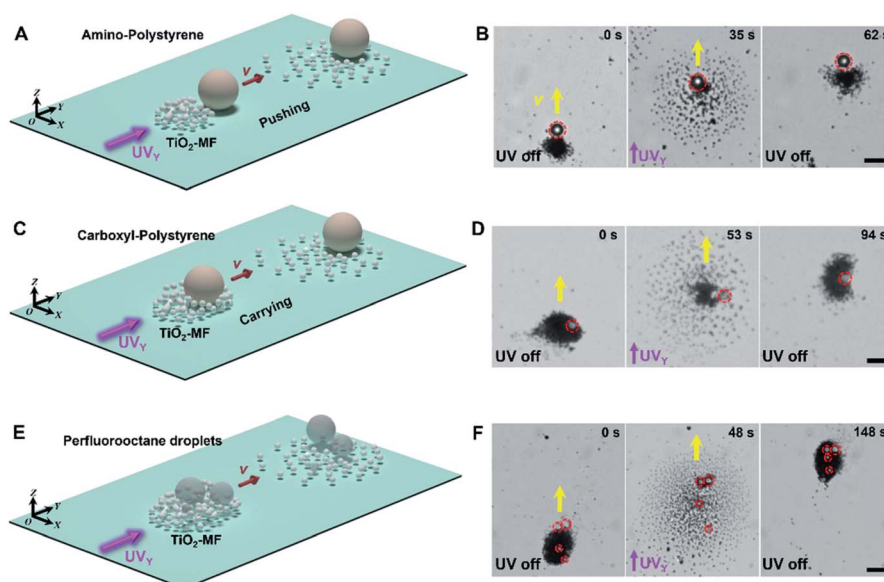
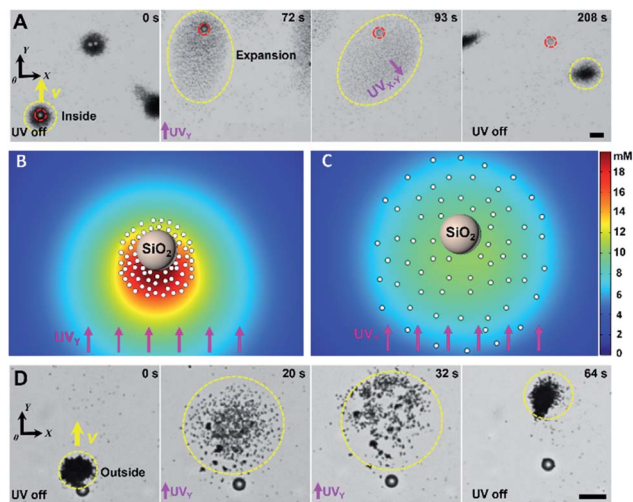


Fig. 3 Cooperative transport of different types of large cargoes by flocking phototactic TiO<sub>2</sub> micromotors. The schematic diagrams and optical microscope snapshots depicting the cooperative transport of an amino-polystyrene microsphere ((A) and (B), *d*: 10 μm), a carboxyl-polystyrene microsphere ((C) and (D), *d*: 10 μm) and perfluorooctane droplets ((E) and (F), the average *d* is 5 μm) by TiO<sub>2</sub>-MFs. The red dashed circles show the positions of the corresponding cargo particles. Yellow arrows indicate the motion direction of the flocks. Images are taken from ESI Video 5.† Scale bars: 10 μm. UV light intensity: 500 mW cm<sup>-2</sup>. H<sub>2</sub>O<sub>2</sub> concentration: 0.25 wt%.



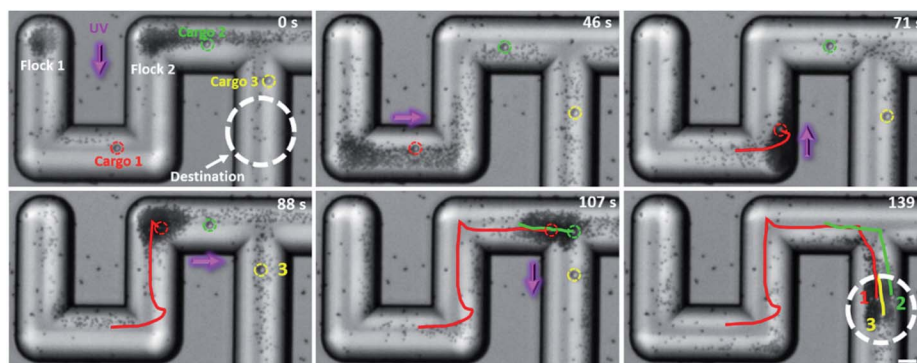


**Fig. 4** Light-controlled large-cargo unloading from  $\text{TiO}_2$ -MFs. (A) Time-lapse optical microscopy images illustrating the unloading of a  $\text{SiO}_2$  microsphere that was inside of a  $\text{TiO}_2$ -MF by disassembling the flock, taken from ESI Video 6.† (B and C) Simulated  $\text{O}_2$  concentration around a passive  $\text{SiO}_2$  microsphere surrounded by 65  $\text{TiO}_2$  micromotors in  $\text{H}_2\text{O}_2$  aqueous solution (0.25 wt%) under UV irradiation ( $500 \text{ mW cm}^{-2}$ ) with different  $L$  of 2.5 (B) and  $6 \mu\text{m}$  (C). The different  $L$  is because of the collective expansion based on nonelectrolyte diffusiophoresis upon UV illumination. (D) Time-lapse optical microscopy images illustrating the unloading of an amino-polystyrene microsphere that was outside of a  $\text{TiO}_2$ -MF by reversing the flock away from the microsphere, taken from ESI Video 7.† Yellow and red dashed circles represent objects of  $\text{TiO}_2$ -MFs and cargoes, respectively. Yellow arrows indicate the motion direction of the flocks. Scale bars:  $10 \mu\text{m}$ . UV light intensity:  $500 \text{ mW cm}^{-2}$ ,  $\text{H}_2\text{O}_2$  concentration: 0.25 wt%.

the experimental results in Fig. 4A and B. For a large cargo that was carried inside of a  $\text{TiO}_2$ -MF, it can be unloaded by disassembling the flock. Specifically, when a  $\text{SiO}_2$  microsphere (as the large cargo,  $10 \mu\text{m}$ ) was carried to the destination under the navigation of the pulsed  $\text{UV}_Y$  irradiation (0–72 s in Fig. 4A), an extra UV light ( $\text{UV}_X$ ) was turned on. Under the superimposed continuous  $\text{UV}_X$  and  $\text{UV}_Y$  irradiation (or the continuous  $\text{UV}_{X-Y}$

irradiation in a direction with an angle of  $45^\circ$  between the  $+X$  and  $-Y$  axis), the  $\text{TiO}_2$ -MF was disassembled into scattered micromotors. With the prolonging irradiation time, the scattered  $\text{TiO}_2$  micromotors moved away from the large cargo (72–93 s in Fig. 4A). Thus, a distinct displacement difference was induced between the  $\text{TiO}_2$ -MF and cargo (93 s in Fig. 4A), and the large cargo was then unloaded because the electrolyte diffusiophoretic attraction became too weak due to the large flock-cargo distance after the  $\text{UV}_{X-Y}$  irradiation was off (208 s in Fig. 4A). The yellow and red dashed circles in Fig. 4A mark the real-time positions of the  $\text{TiO}_2$ -MF and the cargo, respectively, which also record the corresponding unloading process. To decipher the cargo unloading by disassembling the  $\text{TiO}_2$ -MF, we simulated the distribution of the photogenerated  $\text{O}_2$  molecules across the large cargo surrounded by a cluster of  $\text{TiO}_2$  micromotors ( $1.2 \mu\text{m}$ ) with different average motor-motor distances ( $L$ ). With increasing  $L$  from 2.5 (Fig. 4B) to  $6 \mu\text{m}$  (Fig. 4C), corresponding to the different scattered states of the  $\text{TiO}_2$  micromotors under normal  $\text{UV}_Y$  irradiation (72 s in Fig. 4A) and under continuous  $\text{UV}_{X-Y}$  irradiation (93 s in Fig. 4A), the  $\text{O}_2$  concentration gradient across the  $\text{SiO}_2$  microsphere along the  $+Y$  direction decreased sharply, weakening its nonelectrolyte diffusiophoresis (or the subjected diffusiophoretic pushing force from the micromotors). As a result, the  $\text{SiO}_2$  cargo is left behind by the scattered  $\text{TiO}_2$  micromotors and finally unloaded from the  $\text{TiO}_2$ -MF. On the other hand, in the scenario that the large cargo is outside of the  $\text{TiO}_2$ -MF, it would be easier for the cargo to be unloaded. As shown in Fig. 4D, with the UV irradiation pointing in the  $+Y$  direction, the  $\text{TiO}_2$ -MF would move backward away from the carried cargo (an amino-polystyrene microsphere,  $10 \mu\text{m}$ ), and then the cargo was unloaded from the flock successfully.

The transport capability of  $\text{TiO}_2$ -MFs in a confined space was also tested here, as demonstrated in Fig. 5 and ESI Video 8.† When the  $\text{TiO}_2$  micromotors and three large cargoes ( $\text{SiO}_2$  microspheres,  $10 \mu\text{m}$ ) were transferred into a glass microchannel in a rotated S-shape, they formed two flocks at different corners, and the three cargoes (circled by red, green, and yellow circles, respectively) were located at different positions. In the



**Fig. 5** Time-lapse optical microscopy images illustrating the cooperative transport of three large cargoes by  $\text{TiO}_2$ -MFs under the navigation of UV light in a microchannel. The cargoes ( $\text{SiO}_2$  microspheres,  $10 \mu\text{m}$ ) are marked in different colors. The white dashed circles represent the target area. The optical microscope snapshots are taken from ESI Video 8.† Scale bar:  $20 \mu\text{m}$ . UV light intensity:  $500 \text{ mW cm}^{-2}$ ,  $\text{H}_2\text{O}_2$  concentration: 0.25 wt%.



presence of UV<sub>Y</sub> (−Y direction), the two TiO<sub>2</sub>-MFs initiated negative phototaxis toward the same wall and merged into a large flock (0–46 s). In the meantime, cargo 1 was loaded by the TiO<sub>2</sub>-MF. After turning the UV light to +X direction, the merged TiO<sub>2</sub>-MF coercing cargo 1 moved toward the right corner. By a similar approach, the TiO<sub>2</sub>-MF was guided to pass through the “S” microchannel and deliver the cargoes to the pre-designed destination within 139 s. The red, green and yellow lines in Fig. 5 depict the trajectories of cargoes 1, 2, and 3, respectively. The above results reveal the feasibility of cooperative transport in complex landscapes by the flocking TiO<sub>2</sub> micromotors.

## Conclusions

This work has demonstrated that phototactic TiO<sub>2</sub>-MFs can cooperatively manipulate multiple and different types of large cargoes under UV navigation. The swarming and collective phototaxis of TiO<sub>2</sub> micromotors are produced from the spontaneous electrolyte diffusiophoretic attraction and photo-induced nonelectrolyte diffusiophoretic repulsion, which can also be tuned to load, transport, and release large cargoes when controlling the on/off, illumination time and incident direction of UV light. Thus, under UV navigation, multiple and different types of large cargoes can be cooperatively transported along a pre-designed path and be deployed at a predetermined destination in an open space or complex microenvironments. This strategy of cooperative transport may advance the applications of swarming micro/nanomotors in drug delivery, micromanipulation and microengineering.

## Conflicts of interest

There are no conflicts to declare.

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