

Transition between Collective Behaviors of Micromotors in Response to Different Stimuli

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S Supporting Information

ABSTRACT: We report a Ag_3PO_4 microparticle system showing collective behaviors in aqueous medium. Transition between two emergent patterns, namely “exclusion” and “schooling”, can be triggered by shift in chemical equilibrium upon the addition or removal of NH_3 or in response to UV light. The transitions are consistent with a self-diffusiophoresis mechanism resulting from ion gradients. The reported system is among the few examples of nanomotors that are based on a reversible nonredox reaction and demonstrates new design principles for micro/nanomotors. Potential applications of the reported system in logic gates, microscale pumping, and hierarchical assembly have been demonstrated.

Self-organization in living systems leads to the emergence of diverse biological structures. In these systems, transition between emergent behaviors arises from the interactions of individual units in response to the change of local environment. The systems, in turn, are inspiring to the design of micro- or nanomachines that can communicate and cooperate with each other leading to potential applications in the fields of NEMS/MEMS, drug delivery, particle assembly, and chemical sensing.^{1–12}

Synthetic micro- or nanomotors that are powered by chemical catalysis,^{13–23} light,^{24,25} acoustic wave,^{26,27} and electric^{9,28,29} or magnetic field^{30–33} have recently attracted a wealth of interest.^{34–40} However, there are few examples of synthetic motors showing collective emergent behaviors:^{24,41–43} Ibele et al.^{24,42} discovered that AgCl microparticles (MPs) form “schools” when powered with UV, and the motion characteristics these particles depend on the number of other particles surrounding them.⁴⁴ Kagan et al.⁴¹ found that gold microparticles in H_2O_2 solution swarm upon addition of hydrazine. These collective emergent behaviors of synthetic micro/nanomotors are based on the mechanism of self-diffusiophoresis.⁴⁵ In response to a stimulus like light or chemicals, reactions are initiated on the particle surface, generating concentration gradients of ions, which in turn power the motion of the particles themselves.

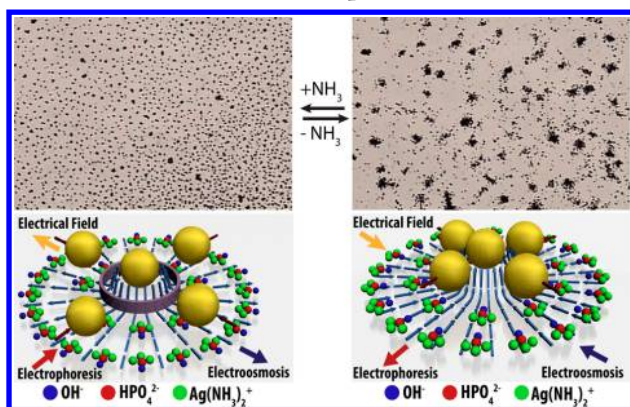
Micro- and nanomotor systems, including those exhibiting collective behavior, are typically based on irreversible reactions. As a result, motion of motor particles is mostly controlled by the supply/drainage of chemical fuels or energy (light, electric or magnetic field). Likewise, the observed collective behavior cannot be *actively* reversed.

Herein we report a new micro/nanomotor system that exhibits reversible collective behaviors in response to several external stimuli: Ag_3PO_4 MPs in aqueous medium show transition between “exclusion” (repulsion-like dispersion) and “schooling” (attraction-like clustering), and the transition can be triggered by shifts in chemical equilibrium (by addition or removal of NH_3) or in response to UV light. The collective behaviors are based on a self-diffusiophoresis mechanism,^{24,41,42} as shown in Scheme 1. The system can work as a NOR gate with NH_3 and UV as inputs, function as a microscale pump, and lead to hierarchical assembly of active (Ag_3PO_4 MPs) and inert particles (0.9 μm PS-carboxylate and 2.34 μm silica tracers). It is also among the few reported examples of synthetic micro/nanomotor systems⁴⁶ that are based on a nonredox reaction and demonstrates new design principles for micro/nanomotors.

Adding 2 mM NH_3 solution, Ag_3PO_4 MPs ($\sim 2 \mu\text{m}$) that sit above a negatively charged glass slide show within seconds an exclusion behavior with exclusion zones formed between particles (Figure 1a). When NH_3 starts to evaporate (~ 3 min), the particles begin to school, forming small clusters (Figure 1b). These clusters then serve as nuclei for larger schools, attracting other nearby particles (Figure 1c,d and Supporting Information (SI) video). Furthermore, the formed schools respond to the chemical trails secreted by other schools and swarm with them to form even larger sized schools (Figure S1 and SI video).

The observed phenomenon is consistent with a self-diffusiophoresis mechanism, in which the motion of particles arises from the concentration gradient of electrolytes generated by particles themselves or their neighbors. For self-diffusiophoresis near a wall (in this case, glass slide), two effects contribute to the motion of the particles:²⁴ electrophoretic/electroosmotic and chemophoretic effects. The former results from the different diffusivities of cations and anions which contribute to the ion gradient in a given direction. The difference leads to a net electric field, which acts both phoretically on the particles and osmotically on the protons adsorbed in the double layer of the negatively charged glass slide. Also, the concentration gradient of the electrolytes causes a gradient in the thickness of the electrical double layer and thus a “pressure” difference along the glass slide. As a result, the solution flows from the area of higher electrolyte concentration to that of lower concentration, which is the chemophoretic effect. The diffusiophoretic speed of particles near a wall in a monovalent salt gradient can be approximated from eq 1:²⁴

Received: December 12, 2012

Scheme 1. Transition between Exclusion and Schooling Behaviors Based on Self-Diffusiophoresis^a

^aWith NH_3 added, OH^- produced by the reaction diffuses away faster from the Ag_3PO_4 MPs than the other ions, resulting in an electric field pointed outward (orange arrow). This leads to inward electrophoresis of the particles (red arrows) and outward electroosmotic flow (blue arrows) along the glass substrate, with the latter dominating resulting in exclusion behavior. With NH_3 removed, the reaction is reversed and so are the effects mentioned above, and schooling behavior is observed.

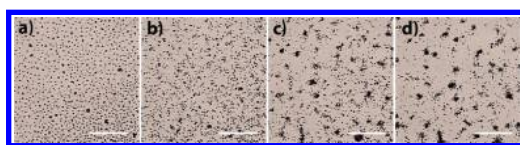


Figure 1. Transition between two emergent behaviors for Ag_3PO_4 MPs. Optical microscope images: (a) exclusion behavior right after addition of 2 mM NH_3 , (b–d) schooling behavior following elapsed time after addition of NH_3 : (b) 3, (c) 5, (d) 7 min (SI video). Scale bar, 50 μm .

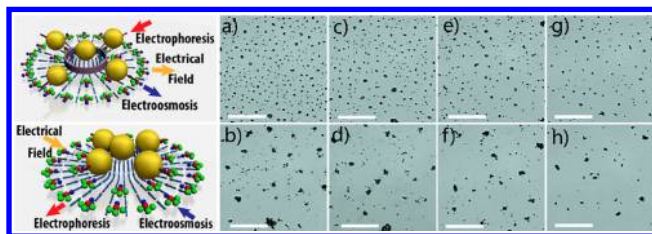


Figure 2. Repeated transition between two emergent patterns for Ag_3PO_4 MPs. Optical microscope images: (a) Adding 2 mM NH_3 , particles show exclusion pattern; (b) removing NH_3 , particles show schooling pattern; (c) further addition of NH_3 switches the system to exclusion pattern; (d) system shows schooling pattern again after certain time with NH_3 evaporation. Cycle is repeated in (e,f) and (g,h). Scale bar, 50 μm . Cycle time scale, ~ 7 min.

$$U = \underbrace{\left[\frac{d \ln(C)}{dx} \right] \left[\frac{D_C - D_A}{D_C + D_A} \right] \left[\frac{k_B T}{e} \right] \left[\frac{\epsilon(\zeta_p - \zeta_w)}{\eta} \right]}_{\text{Electrical Field Term}} + \underbrace{\left[\frac{d \ln(C)}{dx} \right] \left[\frac{2\epsilon k_B T^2}{\eta e^2} \right] \left\{ \ln \left[1 - \tanh^2 \left(\frac{e\zeta_w}{4k_B T} \right) \right] - \ln \left[1 - \tanh^2 \left(\frac{e\zeta_p}{4k_B T} \right) \right] \right\}}_{\text{Chemophoretic Term}} \quad (1)$$

where U is the diffusiophoretic speed of particles, $d \ln(C)/dx$ is the electrolyte gradient, D_C and D_A are the diffusivities of the cation and anion components of the gradient, k_B is the Boltzmann constant, T is the temperature, e is the elementary charge, ϵ is the solution permittivity, η is the dynamic viscosity of

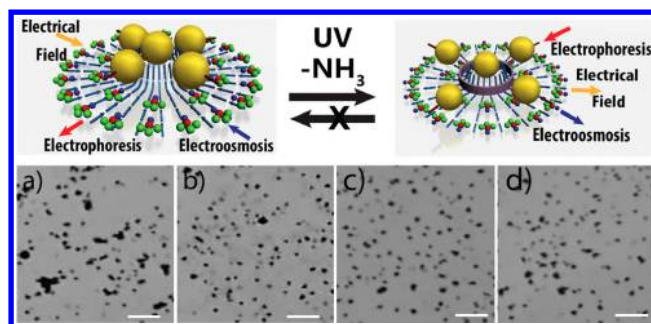


Figure 3. UV effect on Ag_3PO_4 MPs/ NH_3 system. Optical microscope images: (a,b) Transition from schooling to exclusion; with UV addition, schools of Ag_3PO_4 MPs are disassembled and exclusion zones are formed between Ag_3PO_4 MPs. (c–d) UV stops transition from exclusion to schooling; with UV, particles just relax from exclusion behavior with no schools formed within the time period observed (10 min). Scale bar, 20 μm .

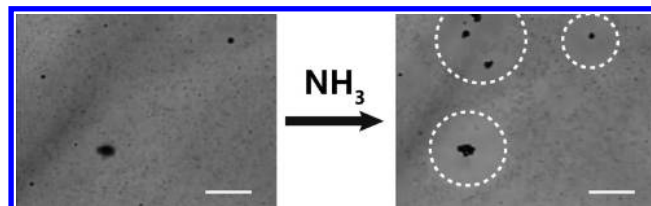
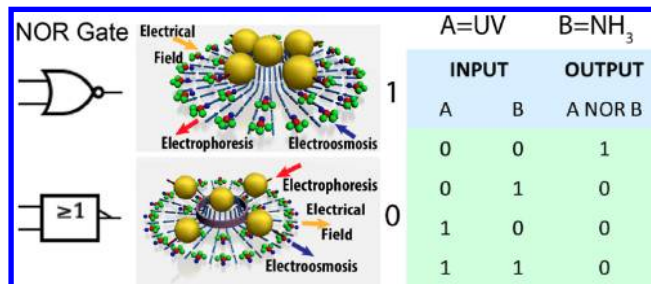
Scheme 2. NOR Gate with UV and NH_3 as Inputs and Collective Behaviors as Outputs: Schooling and Exclusion Behaviors as 1 and 0, Respectively

Figure 4. Optical microscope images of Ag_3PO_4 microscale pump system. Adding 2 mM NH_3 , 0.9 μm PS-carboxylate tracer particles are pumped away from the central pump particles, and exclusion zones (white circled areas) are formed within seconds. Exclusion zone sizes vary from pump particles, and larger ones are found near bigger Ag_3PO_4 MPs. Scale bar, 50 μm .

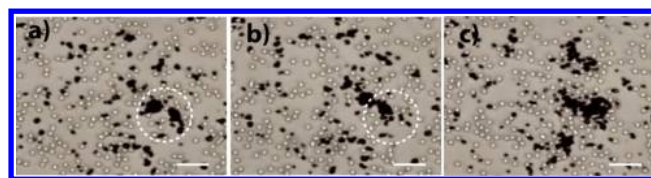


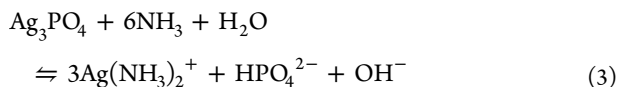
Figure 5. Hierarchical particle assembly between Ag_3PO_4 MPs and 2.34 μm silica tracers. Optical microscope images: (a) Removing NH_3 , Ag_3PO_4 MPs form schools with silica tracers on the outer boundary; (b) when smaller schools start to merge, silica tracers are excluded to the periphery of the newly formed larger schools; (c) Hierarchical particle assembly between Ag_3PO_4 MPs and silica tracers is achieved with Ag_3PO_4 MPs schools as the core and silica tracers on the periphery. Scale bar, 20 μm .

the solution, ζ_p is the zeta potential of particles, and ζ_w is the zeta potential of the wall (glass slide). Since

$$\frac{d \ln(C)}{dx} \approx \frac{dC}{C dx} = \frac{1}{C} \frac{dC}{dx} \quad (2)$$

diffusiophoretic speed drops as electrolyte concentration goes up, as Ibele et al. reported.²⁴

For Ag_3PO_4 MPs with added NH_3 , the following reaction takes place at pH of ~ 10.5 :



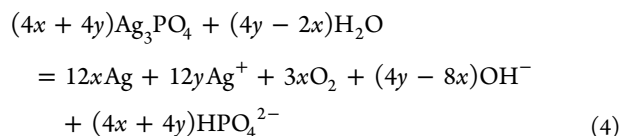
The equilibrium constant of the reaction is 9.1×10^3 , which can be calculated by combining K_{sp} of Ag_3PO_4 and K_f for the $\text{Ag}(\text{NH}_3)_2^+$ complex.⁴⁷ At a low concentration of NH_3 (2 mM), the reaction does not proceed to completion, with $\sim 19\%$ NH_3 left unreacted (calculations in SI).

As NH_3 is added to the system, the equilibrium (eq 3) shifts to the right, generating an ion gradient of $\text{Ag}(\text{NH}_3)_2^+$, HPO_4^{2-} ($D = 0.759 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), and OH^- ($D = 5.273 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), with the highest electrolyte concentration near the particle surfaces. For a given Ag_3PO_4 particle (now considered the central particle), OH^- ion diffuses away from its surface much faster than the rest because of its smaller size, and a net electric field is generated pointing away from the particle.⁴⁵ The electric field acts phoretically on the other negatively charged Ag_3PO_4 MPs by pulling them toward the central one. The electric field also acts osmotically on the adsorbed protons in the double layer of glass slide by pumping the fluid away from the central Ag_3PO_4 particle along the wall. Because the absolute value of ζ potential of the Ag_3PO_4 particle ($\zeta_p = -55 \text{ mV}$) is smaller than that of the glass slide ($\zeta_w = -85 \text{ mV}$),⁴⁸ electroosmosis dominates over electrophoresis, and the other particles are pumped away from the central particle. Although the ζ potential of silver phosphate particles varies with NH_3 concentration, it is still less negative than that of the glass substrate (Figure S2). As for chemophoretic effect, the higher electrolyte concentration near the particle's surface will also drive the other particles away. These effects together cause the Ag_3PO_4 MPs to move away from one another, and the system shows an exclusion pattern (Scheme 1, left).

When NH_3 is removed from the system by evaporation, the equilibrium (eq 3) shifts to the left, as predicted from Le Chatelier's principle. The existing Ag_3PO_4 MPs in the system work as seed crystals with the ions $\text{Ag}(\text{NH}_3)_2^+$, HPO_4^{2-} , and OH^- migrating back, the lower electrolyte concentration being near the particle surfaces. As a result, the electric field points toward the particles, and the situation discussed above is reversed with particles being pumped toward one another to form schools (Scheme 1 right).

To verify that it is the removal of NH_3 that leads to the shift in equilibrium, an experiment was conducted in a closed system, and in this case only exclusion behavior was observed. In addition, when a nonvolatile ligand, ethylenediamine, was employed instead of NH_3 , only exclusion behavior was observed. To further verify the self-diffusiophoresis mechanism, we conducted experiments in presence of high-salt concentrations, since diffusiophoretic motion is sharply attenuated by increasing ionic conductivity of the fluid. By using 0.5, 1, and 3 mM NaNO_3 solutions, we found that schooling propensity decreased with higher electrolyte concentration, as predicted from eq 1 and the simulation results of Sen et al.⁴⁹ (SI video). It is also possible to repeatedly transition from exclusion to schooling behavior and back by sequential addition and removal (evaporation) of NH_3 (Figure 2).

In addition to the transition triggered by equilibrium shift, a transition from schooling to exclusion behavior can also be realized by exposure to UV light. Ag_3PO_4 has been recently shown to have photooxidation properties,⁵⁰ with the following reaction occurring in the presence of UV light:



Thus, upon UV exposure, ions are generated through eq 4, and the faster diffusivity of OH^- leads to an electrical field pointing away from the particle surface, and together with outward chemophoretic effect, exclusion behavior is expected. As a result, with UV addition to an already "schooled" system (Figure 3a), transition from schooling to exclusion behavior takes place with the schools disassembled and exclusion zones formed between particles (Figure 3a,b). In addition, continued UV exposure prevents schooling behavior in Ag_3PO_4 MPs/ NH_3 system: UV light causes the exclusion zones to last longer, and Ag_3PO_4 MPs will only relax to normal state slowly, with no schools formed (Figure 3c,d). This relaxation also suggests negligible contribution from thermophoresis. Thermophoresis is also ruled out by the failure of inert silica particles to exhibit collective behavior in the presence of UV light.

Now that we have two stimuli for the Ag_3PO_4 MPs/ NH_3 system, a NOR gate can be designed with UV and NH_3 as inputs, while schooling and exclusion behaviors as output 1 and 0, respectively. After the formation of schools in the Ag_3PO_4 MPs/ NH_3 system, without inputs of UV or NH_3 , the schooling behavior results with NH_3 removal and "1" as the output, while any input, either UV or NH_3 , causes a shift to exclusion behavior and output of "0" (Scheme 2). The NOR gate design, as shown by Pierce, can be used to reproduce the functions of all the other logic gates⁵¹ and therefore perform any logical operation required.

In addition to interaction between Ag_3PO_4 MPs, interaction between active Ag_3PO_4 MPs and inert negatively charged tracer particles was also investigated. Again, when NH_3 was added to the system, equilibrium (eq 3) shifts to the right, and the resulting ions secreted from the active Ag_3PO_4 MPs particles generate diffusiophoretic flows that cause exclusion zones to form between not only active particles but also active and inert ones (here, $0.9 \mu\text{m}$ PS-carboxylate tracer particles). As a result, the PS-carboxylate tracers are pumped away from the bulky Ag_3PO_4 MPs that sit on the glass slide. Also, probably due to the difference in reactivity, the size of exclusion zones formed increase with increasing size of the Ag_3PO_4 "pump" particles (Figure 4, SI video). On the other hand, with NH_3 removed from the system, the ion concentration gradient and the directions of diffusiophoretic flow are reversed. As a result, the active silver phosphate particles attract each other as well as the silica tracers and form schools. It is interesting to note that the inert silica tracers mainly sit on the outer boundary of the formed schools, and when the smaller schools start to fuse, the silica tracers that are on the merging boundaries are "excluded" to the periphery of the newly formed larger school. Thus, with smaller schools merging altogether, hierarchical particle assembly between active Ag_3PO_4 MPs and inert silica tracers is achieved (Figure 5, SI video).

In conclusion, we have demonstrated a new reaction-induced self-diffusiophoresis system, in which two different collective

behaviors, exclusion and schooling, can be attained using either a chemical or light stimulus. This system is also the first example of micromotors based on a nonredox chemical equilibrium shift and demonstrates new principles for micromotor design. The system has potential applications in the fields of microscale pumping and hierarchical particle assembly. In addition, micromotors with different stimuli may be employed as logic gates.

■ ASSOCIATED CONTENT

📄 Supporting Information

Materials, experimental procedures, 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.

■ ACKNOWLEDGMENTS

Research was supported by the NSF (DMR-0820404, CBET-1014673).

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