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Microparticles

Chemically Triggered Swarming of Gold Microparticles**

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The collective behavior of animals, such as the swarming of bees or schooling of fish, is widely observed in nature. Inspired by animal interactions, the autonomous movement and collective behavior of synthetic nanomaterials are of considerable interest as they have implications for the future in nanomachinery, nanomedicine, and chemical sensing.[1–4] Recently, Whitesides and co-workers[3] illustrated macroscale self-assembly of self-propelled hemicylindrical plates induced through capillary and chiral interactions. Sen et al. and Mallouk and co-workers examined the microfluidic, electrokinetic pumping of tracer particles on bimetallic (Au/Ag or Au/Pd) surfaces as a result of the catalytic decomposition of hydrogen peroxide or hydrazine fuels.[2c,5] The same groups recently exploited a light-induced self-diffusiophoresis phenomenon for the schooling of inert SiO_2[4] or AgCl[5] particles and for the propulsion of TiO_2 and SiO_2/TiO_2 Janus particles.[6] These recent examples indicate the potential to induce swarming of synthetic micro-objects outside living systems.

Herein we demonstrate the ability to organize Au microparticles (Au MPs) in discrete regions by using an electrolyte gradient triggered by adding hydrazine to a hydrogen peroxide solution. We illustrate that the size and shape of the Au MP swarms and the rate of such school formations can be tailored by modifying the catalytic gold surface (with different alkanethiols) or by controlling the MP concentration. This chemically triggered particle organization can also be reversed and repeated through subsequent additions of hydrazine. We present a hypothetical model for a diffusiophoretic swarming mechanism that is supported by the observed aggregation behavior of Au MPs. Overall, the observed aggregation is both scalable and versatile enough to be expanded into using biological redox species for the purpose of creating 'intelligent' artificial nanomachines.

Unlike earlier light-driven diffusiophoretic swarming[4–7] (involving particle degradation into ions and radicals), the presented chemically induced swarming is the first to rely on intact, monocomponent Au MPs to catalyze redox reactions. Au MPs in a hydrogen peroxide solution, spiked with hydrazine, move autonomously at speeds up to 16 $\mu m\,s^{-1}$ (see Video 1 in the Supporting Information). This autonomous motion is caused by the localized electrolyte gradient which results from the diffusion of ionic species generated from the surface-catalyzed decomposition of hydrazine and hydrogen peroxide. Such a triggered reaction and electrolyte gradient[4–8] lead to a temporal and spatial organization of Au MPs. Figure 1 displays time-lapse images showing the gradual

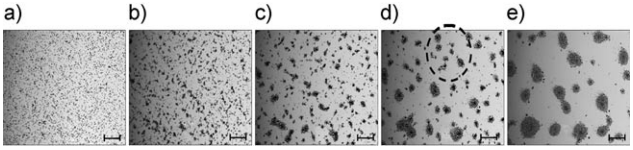

Figure 1. Chemically triggered time-dependent organization of Au MPs. Time-lapse optical microscope images demonstrating chemically hydrazine induced swarming behavior of unmodified Au MPs (5 $mg\,mL^{-1}$) in a 10% H_2O_2 aqueous solution. a) Without hydrazine and (b–e) for different times after adding hydrazine: b) 1 s, c) 5 s, d) 10 s and e) 30 s. (See Video 1 in the Supporting Information). Scale bar, 50 μm. The dynamic merging of smaller schools present in the circled area (d) is shown in Supporting Information Figure S1.

formation of Au MP swarms in response to the addition of hydrazine. The electrolyte gradient instantly leads to the formation of small (ca. 5 μm) Au MP clusters within 1 second (Figure 1 b). The initial formation of 'nuclei' particle clusters draw in neighboring particles to form small swarms which are approximately 15–25 μm wide (Figure 1 c). As seen in Figures 1 d,e and in Video 2 in the Supporting Information, these clusters continuously draw in more particles, resulting in larger schools that are hundreds of microns in diameter. A close-up view (Figure 1 d, circled region) of the dynamic merging of smaller swarms into a larger swarm is illustrated in Figure S1 and Video 3 in the Supporting Information. Here, smaller swarms are attracted to larger ones, which are expected to produce significantly more ions and hence a larger electrolyte gradient.

The chemically triggered swarming of Au MPs results from the diffusion of ionic products from the catalytic Au surface. The reaction between H_2O_2 and hydrazine catalyzed by the gold surface generates H^+, $N_2H_5^+$, and OH^- ions (see equations below).[9] In any given direction, the diffusion rate of these ionic products ($D_{H^+} = 9.311 \times 10^{-5}\,cm^2\,s^{-1}$, $D_{OH^-} = 5.273 \times 10^{-5}\,cm^2\,s^{-1}$, and $D_{N_2H_5^+} = 1.571 \times 10^{-5}\,cm^2\,s^{-1}$) vary relative to each other, thereby forming an electric field.[4,6] From a mechanistic point of view, we speculate that the resulting electric field acts phoretically on the nearby Au MPs, pulling the particles towards the center of the swarms, where the largest electrolyte gradient exists. This field also acts electroosmotically on the nearby walls of the glass slide, resulting in the micropumping of fluids towards the ion-

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producing Au MPs. Overall, the aggregation of the Au MPs, induced by the surface formation of ionic products, resembles the secretion of signaling molecules by animals.

The swarming of Au MPs is not observed in the presence of either hydrogen peroxide or hydrazine alone, reflecting the requirement for the ionic gradient generated from the chemical reactions. Hence, examining the reaction between these constituents in the presence of Au MPs leads to the diffusiophoretic model discussed below. In water, hydrazine dissociates into $N_2H_5^+$ and OH^-, as shown in Equation (1):

$$N_2H_4 + H_2O \rightarrow N_2H_5^+ + OH^- \qquad K_b = 1.3 \times 10^{-6} \tag{1}$$

Initially, hydrazine is diluted 1000-fold in deionized water. With a $K_b = 1.3 \times 10^{-6}$ we estimate that there is a considerable generation of $[N_2H_5]^+$ and OH^- in the basic solution (pH 9.5). When hydrazine is added to hydrogen peroxide, the mixture is likely to undergo a redox reaction where hydrazine is oxidized and peroxide is reduced, according to Equations (2) and (3):[10]

$$N_2H_5^+ \rightarrow N_2 + 5\,H^+ + 4\,e^- \qquad E^\circ = 0.23\ V \tag{2}$$

$$H_2O_2 + 2\,H^+ + 2\,e^- \rightarrow 2\,H_2O \qquad E^\circ = 1.776\ V \tag{3}$$

The pH change associated with the redox reaction between hydrogen peroxide and hydrazine has been monitored over time in the presence and absence of Au MPs (Figure 2a). The data clearly indicates the critical role of Au MPs as a catalytic surface. A rapid decrease of the pH value from 7.6 to 5.8 is observed (within 4 min) in the presence of these MPs, compared to the minimal change (from 7.6 to 7.4) in their absence. We speculate that Au MPs kinetically facilitate the coupled reactions in Equations (2) and (3) because of the thermodynamically favorable net E° value, thereby leading to a dramatic increase in $[H^+]$.

Our hypothesis about this swarming is consistent with the predictions made from a diffusiophoretic model based on the radial diffusion of ions[6] (see the Supporting Information for details). The model examines changes in the proton concentration at the center of a finite particle cluster. It is calculated that within a few milliseconds the proton concentration at the center point increases to nearly fivefold compared to the initial concentration on the particle surface (Figure 2b). The model takes into account changes in the proton concentration over time and the particle distance from the center point. Particle movement towards the central point for a two millisecond period (Figures 2c–f), drastically increases the difference in proton concentration by more than 330% compared to stationary particles. Such behavior is consistent with the observations documented in Videos 2 and 3 in the Supporting Information, including continuous swarming, large-swarm movements, and smaller swarms attracted to larger swarms. Since the interaction between particles plays a larger role, the model also determines that the proton concentration build-up between only a few particles would not favor attraction (see Video 1 in the Supporting Information).

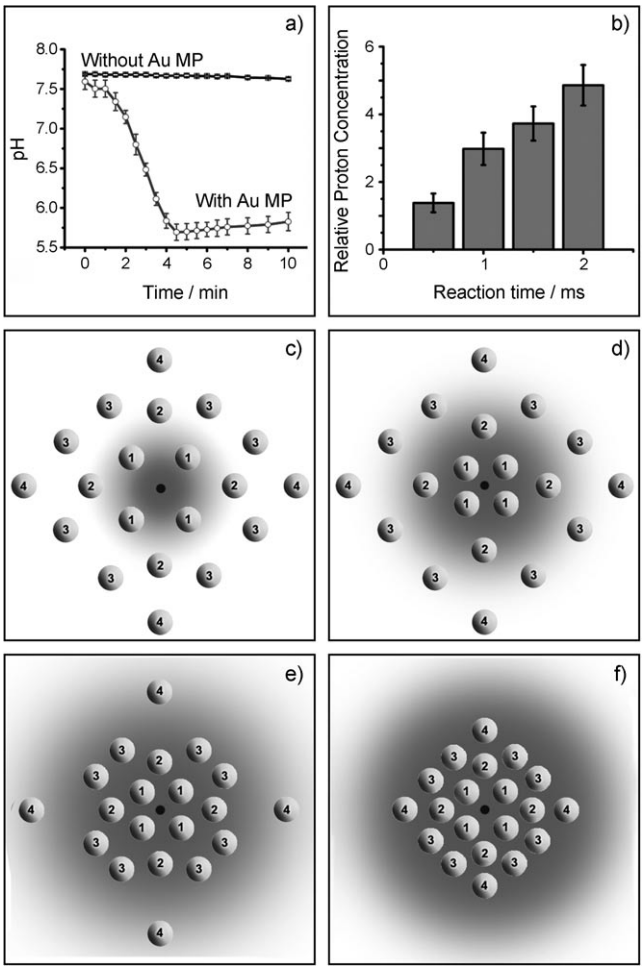

Figure 2. a) pH variation of the 10% H_2O_2–0.01% hydrazine mixed fuel solution with and without Au MPs. b) Calculated increase in the proton concentration at the black center point over time with respect to the concentration on the particle surface. (c–f) Time-lapse schematic of Au MPs swarming (0.5 ms intervals) shown by the grayscale gradient, as predicted by the diffusiophoretic model. Error bars, 1 standard deviation.

Although the school formation is not a permanent process, it is highly reversible and repeatable, with defined transitions between the dispersed and grouping states (see Video 4 in the Supporting Information). After a given time the schools start to lose their shape and density, and eventually the Au MPs disperse evenly across the slide (Figures 3c and e). This loss of aggregation is attributed to the depletion of hydrazine which prevents additional ion formation (necessary for the particle swarming). Repeated spiking of the solution with hydrazine leads to renewed school formation (Figures 3b,d,f) until the second (peroxide) component is consumed. The sudden drop and leveling of the pH curve (Figure 2a) correlates well with the initiation and hydrazine consumption part of the swarming cycle. In general, the time for a swarm formation/dissipation cycle varies with the concentration, as a higher concentration of Au MPs ($5\ mg\,mL^{-1}$) takes half the time (20 min) compared to a 10-fold diluted MP solution. This is most likely attributed to the decreased ionic gradient and larger interparticle spacing,

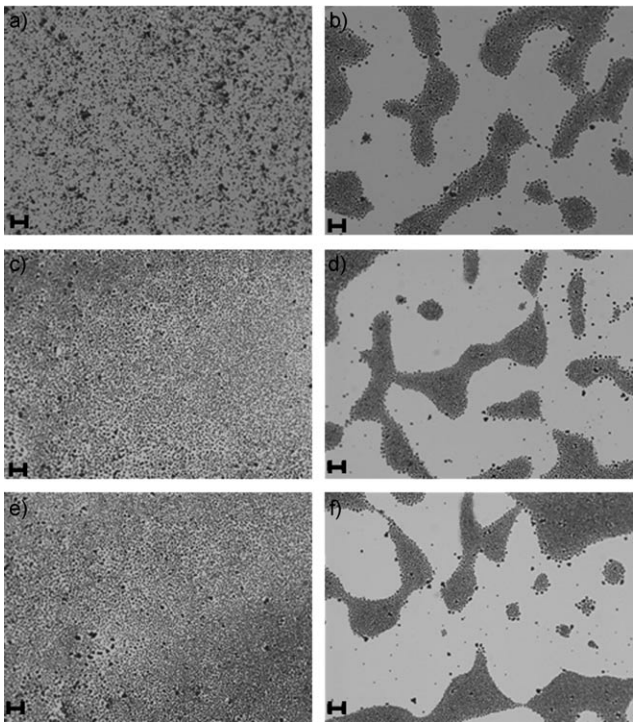

Figure 3. Reversible swarm formation of unmodified Au MPs induced by repetitive hydrazine additions. a) Before hydrazine spiking and b) one min after addition. Once the schools dissipate hydrazine is added (c) and the Au MPs reform into schools (d). This cycle is repeated again in (e) and (f). Scale bar, 20 μm.

charged coating (Figure S4 d). Such ability to tailor the catalytic activity of the surface (through judicious coating), and thus to manipulate the collective behavior of metal microparticles, holds promise for designing 'intelligent' synthetic nanomachines.

Furthermore, we exploited the scalability of this diffusiophoretic phenomenon by monitoring the defined swarming of Au MPs and "inert" silica particles around large 100 μm patterned gold disks. The data in Figure 4 and in the corresponding Video 5 in the Supporting Information reveal

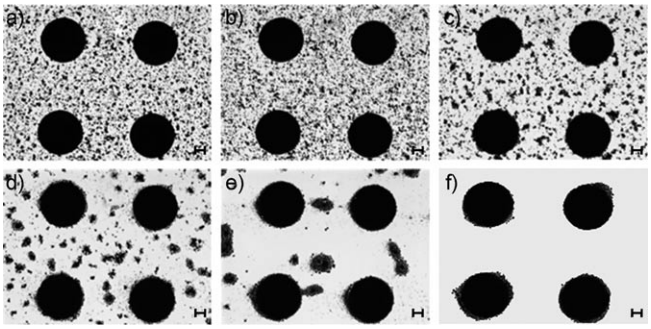

Figure 4. Controlled swarming of Au microparticles. Time-lapse images depicting the progression of concentrated particle swarming towards 100 μm gold disks. Particle swarming is seen to progress at a) 0, b) 1, c) 5, d) 10, e) 30, and f) 60 s after adding the mixed fuel. Scale bar, 20 μm.

which leads to smaller schools and delayed swarming (see Figure S2 in the Supporting Information).

Controlling the surface chemistry of the Au MPs can be used for tailoring the rate of ion formation ("secretion") and hence the extent of the corresponding pH value change and electrolyte gradient. The data in Figure S3 in the Supporting Information demonstrates how aminothiol-modified Au MPs ($\xi = +15.5$ mV, Figure S3B) and mercaptoundecanoic-acid-modified Au MPs ($\xi = -25.2$ mV, Figure S3C) influence the school formation two minutes after the hydrazine addition. Unlike the unmodified Au MPs (Figure S3A), the different surface modifications resulted in smaller schools. Positively modified particles did not repel each other, suggesting that the school formation may also be influenced by ion-flux-induced electroosmotic flows.[4] As expected, the negative surface modification led to tightly packed schools of the Au MPs (Figure S3C). However, this formation was temporary as larger schools, typical of unmodified particles, were eventually formed. The delayed school formations were attributed to the slow reaction kinetics on the modified gold surfaces. This trend was confirmed by measurements of the solution pH values which indicate a delayed pH value decrease on the coated particles. The data is shown in pH/time profiles for the Au MPs coated with different alkanethiols (see Figure S4 in the Supporting Information). Different temporal profiles are observed, reflecting changes in the reaction kinetics. As expected, the fastest pH value change is observed for the solution containing the uncoated Au MPs (Figure S4 a) and the slowest pH decrease is observed using the negatively

the controlled directional swarming of Au MPs in the presence of hydrogen peroxide and hydrazine. As can be observed in the video and from these time-lapse images, the 100 μm Au patterned surfaces emulate bigger swarms by creating large ionic gradients, which predictably collect the surrounding Au MPs. Such behavior appears to mimic the swarming of bees around a desired food source. As a result of the electroosmotic pull from the ionic movement this behavior has also been observed using noncatalytic (silica) particles (see Video 6 in the Supporting Information), thereby making it versatile for diverse applications, ranging from nanoparticle pickup to micropumping.

In summary, we have demonstrated the swarming behavior of Au MPs in response to chemical stimuli. Such ability to organize Au MPs in discrete regions reflects the asymmetric movement of ionic reaction products generated ("secreted") at the Au catalyst surface and the resulting electrolyte gradient. The size and shape of the metal MP swarms can be controlled by modifying the particle surface (with different alkanethiols) or by controlling the density of particles. The swarming of the Au MPs can be reversed (with defined transitions between the dispersed and grouping states) through repetitive hydrazine additions. Furthermore, we show that these behaviors work on both the micro- and macroscale. This swarming phenomenon can be used to model the collective behavior of future nanomachines or nanosized objects in connection with other redox species and catalytic particles. The ability to regulate the collective behavior of synthetic microscale particles (by controlling

the surface coating) is promising for the creation of 'intelligent' nanomachines that perform collective tasks.

Experimental Section

Commercially available pure gold microparticles (Au MP, 0.8–1.5 μm, 99.96 + %) were purchased from Alfa Aesar. Mercaptoundecanoic acid (MUA) was purchased from Sigma while 11-amino-1-undecanethiol is purchased from Dojindo Molecular Technologies. For modification of Au MP with different alkanethiols, 1 mg mL^{-1} of as received particles were initially washed three times with water and absolute ethanol. The particles were subsequently incubated with 10 mM alkanethiols solution for 18 hrs followed by repeated washing with absolute ethanol and final redispersion in water. Zeta potentials were measured using Zetasizer Nano (Malvern Instruments, Westborough, MA) in 10 % H_2O_2.

In a typical experiment, the desired concentration of Au microparticles (MPs) was mixed with a H_2O_2 solution (5 μl of a 30% aqueous solution) and placed on a clean cover slide before hydrazine spiking. Final concentrations of 10 % H_2O_2 and 0.01 % hydrazine were used in all of the above experiments. Particle interactions were imaged using an inverted optical microscope (Nikon Instrument Inc., Eclipse TE2000S) equipped with a 20X objective. Photometrics CoolSnap HQ^2 camera (Roper Scientific, Duluth, GA) controlled by NIS-Elements (v3.0) software were used to acquire movies at the frame rate of 15 frames per second. Videos of particle behaviors were captured for additional analysis. The change in pH values of the solution mixture containing 1.6 mg mL^{-1} of unmodified and modified Au MPs was measured using a calibrated pH meter (Fisher Scientific). Aggregation of Au and silica microparticles around 100 μm gold disks was performed under similar fuel. The fuel conditions used for the schooling of particles around the 100μm gold disk (see videos 5 and 6 in the Supporting Information) are the same as in all of the other experiments.

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