Chemical Nanomotors at the Gram Scale Form a Dense Active Optorheological Medium

Udit Choudhury, Dhruv P. Singh, Tian Qiu, and Peer Fischer*

A characteristic feature of living systems is the presence of non-equilibrium assembly as a route to self-organize. For example, bacterial colonies can self-organize into rotating swarms,[1] and microtubule-motor protein systems form aster like formations.[2] These processes are driven by the dissipation of a chemical fuel, such as ATP, to gain motility and induce structural changes.[3–6] This permits the system to evolve into different nonequilibrium states as a function of the fuel consumption. Such a system is, in the case of a fluid-like medium, known as an “active” or “living” suspension.[7] A key feature of these active systems is that they can give rise to interesting collective effects that arise due to interactions between the active units as well as through hydrodynamics at high density.[8,9] For instance, the collective motility of a bacterial suspension can change the bulk viscosity of the suspension,[10,11] and ATP-driven actin–myosin systems show changes in the microstructural phase and its rheological properties that control the mechanical properties of cells.[12,13] Examples of such large scale collective behaviors in synthetic active colloids have been experimentally demonstrated in electrically powered Quincke “rollers”[9,14] and metal-coated colloidal particles[8,15] or by magnetic colloids.[16,17] However, it has been challenging to realize this in large volumes and at high density with artificial chemically active systems. Interesting material properties have been predicted for active colloids at high density, such as a reentrant phase behavior, dynamic pattern formation, and active turbulence that have the potential to form new active materials, but there have been very few suitable experimental systems that permit one to observe these phenomena.[18–22] Moreover, most of the conventional active colloidal systems are either confined to two dimensions or are operated at low densities, and hence are unable to drive changes in the bulk. Here, we show that inorganic chemically-active nanomotors can be used to prepare large volumes of an active medium, whose bulk viscosity can be controlled by the activity of its constituents. This is, to the best of our knowledge, a first demonstration of collective behavior of synthetic active matter giving rise to a tunable change in bulk material property.

Inorganic chemically active colloids or nanomotors convert fuel available in the solvent to self-propel. Due to the asymmetric distribution of catalyst near the colloid, the reaction gives rise to a concentration gradient of product (and educt) molecules or ions across the particle. This causes fluid motion and a slip flow across the particle, and the propulsion of the particle in the opposite direction to the induced slip flows. While several model synthetic active systems are known, including catalytically active Janus particles,[23–32] it has thus far been difficult to obtain truly large numbers of chemical motors to form an active medium and operate them stably for an extended period of time.[23,33,34] The conventional approach to realize an asymmetric distribution of a catalyst on each colloid is to fabricate “Janus” particles, that have a reactive and nonreactive material on each of the particle’s two faces.[24] Physical vapor deposition (PVD) and electro-chemical anodic aluminum oxide (AAO) templated synthesis are commonly used to fabricate Janus particles.[25,26,31,35] However, since both the processes are limited to a monolayer of particles, the overall yield is always low. In addition, pickering emulsion or biphasic electrochemistry based techniques had been used for the bulk synthesis of Janus colloids.[36–39] Here in this study, a simpler alternate strategy is employed to obtain large numbers of catalytically active self-propelling...
particles. The natural shape anisotropy found in the irregularly shaped powder particle is exploited as it gives rise to self-phoresis. We use anatase TiO\textsubscript{2} powders as these are photocatalytic and therefore permit the optical control of their activity. The catalytic reaction causes concentration gradients around the nanoparticles that produce diffusiophoretic effects, which makes them self-propel as well as induce attraction to other nearby particles. Further, we use a biocompatible fuel that scavenges oxygen (a reaction product) and renders the reaction system stable at high particle densities. We show that the bulk viscosity of the active suspension can be changed reversibly with light by an order of magnitude. The use of active powders allows us to demonstrate a novel optorheological medium and paves the way for truly large scale applications of synthetic active matter.

The anatase TiO\textsubscript{2} colloids used herein have an irregular shape (Figure 1a, inset) and a median size of 400 nm (Figure S1a, Supporting Information). As a fuel, we use an aqueous mixture of Tempol (4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl). Unlike, the fuels hydrogen peroxide, hydrazine, or quinone, which are unstable and hazardous chemicals, Tempol can be handled in large scales and is biocompatible. Since Tempol is also an oxygen scavenger, it suppresses the formation of gaseous bubbles and keeps the reaction mixture stable for long periods of time. On illuminating the suspension with UV light, TiO\textsubscript{2} produces electron–hole pairs. The holes react with hydroxide ions to produce hydroxyl radicals. Tempol reacts with the radicals and is converted to Tempone (4-oxo-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl). Oxygen is consumed in the reaction. Since Tempol is also an oxygen scavenger, it suppresses the formation of gaseous bubbles and keeps the reaction mixture stable for long periods of time. On illuminating the suspension with UV light, TiO\textsubscript{2} produces electron–hole pairs. The holes react with hydroxide ions to produce hydroxyl radicals. Tempol reacts with the radicals and is converted to Tempone (4-oxo-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl). Oxygen is consumed in the reaction. Since Tempol is also an oxygen scavenger, it suppresses the formation of gaseous bubbles and keeps the reaction mixture stable for long periods of time. On illuminating the suspension with UV light, TiO\textsubscript{2} produces electron–hole pairs. The holes react with hydroxide ions to produce hydroxyl radicals. Tempol reacts with the radicals and is converted to Tempone (4-oxo-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl). Oxygen is consumed in the reaction.

Figure 1. Motion of shape-asymmetric TiO\textsubscript{2} colloids. a) Image of anatase commercial TiO\textsubscript{2} powder. Scale bar is 1 mm. Inset: scanning electron microscopy (SEM) image of TiO\textsubscript{2} colloids showing the asymmetric shape of the colloids. Scale bar is 1 \(\mu\)m. b) Brownian motion without ultraviolet (UV, 365 nm) illumination. c) Active motion of colloids on illumination by UV light. Scale bar is 5 \(\mu\)m. d) TiO\textsubscript{2} particles join to form clusters. The colored contours mark three such clusters. e) The three colored clusters join to form larger clusters. f) On turning off illumination, the clusters melt and particles disperse. Scale bar in (d), (e), and (f) is 5 \(\mu\)m.
clustering behavior with unstable aggregates that dynamically form and dissociate. The same mixture at a higher light intensity forms larger stable aggregates that self-organize towards an arrested network of colloids (Movie S7, Supporting Information). On switching off the activity (turning the UV light off), all mixtures return to their nascent state (Movie S8, Supporting Information). We also investigated the dynamics at lower density of active particles. We prepared a suspension of 3.5% (v/v) fumed silica with 1.25% (v/v) TiO$_2$. A dispersed phase remains at lower light intensities (Figure 2c), while at high light intensity we find a small isolated cluster phase due to competition between attraction and self-propulsion (Figure 2d and Movie S9, Supporting Information). We used differential dynamic microscopy (DDM)\cite{47-50} (Note S3, Supporting Information) to study the dynamics with bright-field microscopy and extract the structural evolution from the videos. Figure S3a and Figure S3b in the Supporting Information show the decay of intermediate scattering function $f(q, \Delta t)$ is faster at low light intensity ($I = 20$ mW cm$^{-2}$) than for higher light intensity ($I = 200$ mW cm$^{-2}$). Decay of $f(q, \Delta t)$ with a larger slope indicates faster particle rearrangements. At lower light intensities with dynamic clustering, the structure loses its integrity and relaxes faster. At higher intensity with larger inter-particle attractive interactions, the structure progresses towards a clustered arrested-like state which is maintained for longer lag times. Hence, $f(q, \Delta t)$ decays with a smaller slope. From these measurements, it is clear that the microstructural dynamics of this active colloidal suspension can be controlled by tuning the activity (by adjusting the UV light intensity). Further, in the absence of activity, the suspension reverts to its Brownian state. It is expected that this change will be reflected in the microstructure and viscosity of the suspension.

Movie S10 in the Supporting Information shows a magnetoc microprobe rotating in an applied field at 0.5 Hz, while the UV light is on. Suspension of 3.5% (v/v) fumed silica and 2.5% (v/v) TiO$_2$ in 500 $\times$ $10^{-3}$ m Tempol was used for this measurement. Figure 3 shows snapshots of the motion of the microprobe. We find as the microstructure changes with time from a dispersed to an arrested phase, the microprobe's rotation slows down and ultimately stops. It follows that such a microstructural change would also result in a change of viscosity for the entire suspension. The network strength of the

Figure 2. Phase behavior of mixtures. a,b) Mixture of 3.5% (v/v) fumed silica with 2.5% (v/v) TiO$_2$ in 500 $\times$ $10^{-3}$ m Tempol: a) low (20 mW cm$^{-2}$) and b) high (200 mW cm$^{-2}$) light intensity. c,d) Mixture of 3.5% (v/v) fumed silica with 1.25% (v/v) TiO$_2$ in 500 $\times$ $10^{-3}$ m Tempol: c) low (20 mW cm$^{-2}$) and d) high (200 mW cm$^{-2}$). Scale bar is 5 $\mu$m in all figures.
active suspension as a function of activity (light intensity) can be deduced with the help of magnetic microrheology.[10,51] With activity, the inter-particle interaction forces increase and the tendency of the particles to form a stable clustered network will therefore also increase. This is reflected in the increased torque required to rotate the microprobe. Consequently, the local viscosity of the suspension increases and is observed to change eightfold as a function of light intensity (Note S4 and Figure S4 in the Supporting Information).

From these observations, it follows that activity can locally induce a microstructural change, which has been theoretically predicted, but has thus far not been observed.[20] Because of the nature of our active particles, we can now easily scale up the volume of the suspension to examine bulk effects.

To ensure that the structural change does occur throughout the suspension, we recorded images at different heights inside the sample where the particles are far away from the walls. In order to facilitate imaging, we lowered the particle density to 0.6% (v/v) TiO$_2$. The illumination from below provides an additional upward force[45] on the active colloids due to self-shadowing effect of the colloids.

**Figure 4** shows positions of local clusters after illumination for 180 s at different heights. The fractal dimensions of the clusters are analyzed in Table S1 in the Supporting Information. We independently confirmed with long time (200 s) oscillatory strain control experiments of the active suspension without UV illumination that the viscosity remains constant and sedimentation does not play a major role during the course of the measurements (Figure S5 and Note S5, Supporting Information). Further, control measurements of a passive particle suspension of 3.5% fumed silica with 2.5% SiO$_2$ beads (500 nm) and 500 $\times$ 10$^{-3}$ M Tempol under UV illumination revealed a very small irreversible increase in viscosity due to heating induced solvent evaporation (Figure S6 and Note S6, Supporting Information).

A commercial rheometer with a 35 mm parallel plate geometry at 100 $\mu$m gap was then used in its oscillation mode to measure the bulk rheological properties of a dense medium. A custom-made UV light-emitting diode (UV LED) array (see the Experimental Section) illuminates the sample through a glass window from the bottom. The spatial arrangement of the LED array is designed to ensure uniform illumination in the measurement area. The same suspension (3.5% fumed silica with 2.5% TiO$_2$ with 500 $\times$ 10$^{-3}$ M Tempol) as in the microrheological measurements was used for bulk rheology. First, we conducted an oscillatory strain amplitude ($\gamma$) sweep at a frequency of 1 Hz for both active (with UV) and passive (without UV illumination) suspensions (Figure 4b). The passive suspension shows a low viscosity. The slight decrease in the viscosity at higher strain rates could be due to a slight loss in internal structure as the entangled fumed silica particles get pulled apart.[52] In contrast, a much more dramatic effect is seen when the suspension is active under UV illumination. At low strain amplitudes, the viscosity of the suspension increases by an order of magnitude. At higher strain amplitudes, the viscosity decays to the viscosity of the passive mixture. From our microscopic observations, we understand that the dispersed TiO$_2$ colloids form local clusters that give additional structural stability to the suspension. This results in a viscosity increase at low strain amplitudes. At large amplitudes, the networks break and the viscosity approaches that of the passive suspension. Up to $\gamma = 0.1$, i.e., 10% strain, the viscosity remains independent of the strain amplitude. In order to demonstrate that the active state is fully reversible, we performed measurements at a fixed strain amplitude $\gamma = 0.1$ and constant frequency of...
1 Hz and switched the UV light on and off for a period of time. Figure 4c shows that the viscosity is low in the initial 70 sec without activity (UV illumination) and then sharply increases as the system is active. As the light is switched off, the activity ceases and the viscosity returns to its nascent state. The viscoelastic modulus $|G^*|$ also follows a similar trend as can be seen in Figure S7 in the Supporting Information. Thus, the active suspension undergoes a completely reversible change in viscosity by an order of magnitude. Furthermore, by cycling the UV illumination, the viscosity can be changed multiple times as shown in Figure 4d. We also investigated the suspension characteristics at a higher base viscosity of 30 mPa s by using mixture of 5% fumed silica with 2.5% TiO$_2$ in $500 \times 10^{-3}$ M Tempol. The suspension viscosity was found to vary between 30 and 55 mPa s for each illumination cycle (Figure S8, Supporting Information).

We have fabricated an active suspension that consumes fuel from its solvent to form an optorheological medium that undergoes dynamical and structural transformations leading to reversible changes in its rheological properties. The active units of this system are shape-asymmetric anatase TiO$_2$ colloidal powder particles that self-propel in the presence of a Tempol solution. At higher densities, the system shows clustering and aggregation leading to network formation and finally an arrested state. Further, being light controlled, the activity can be externally tuned. Microrheology confirms that microstructural changes underlie the viscosity changes of the active suspension. Measurements conducted in a bulk rheometer demonstrate...
that the active colloids cause reversible, optically-triggered viscosity changes. Thus the collective behavior of the system of active colloids determines the bulk properties of the suspension. In contrast to biological active suspensions, that shows a dynamic steady state, our system progresses toward an arrested steady state at high activity (light illumination).

We note that previous simulations showed that both self-propulsion and attractive inter-particle interactions can independently induce phase separation and clustering. However, in our system, it is difficult to investigate these effects independently as increased activity leads to both increased propulsion and stronger inter-particle interactions. So, the final state of the suspension depends on the relative strength of self-propulsion and inter-particle attraction. We find, that with increasing density and chemical activity, the relative importance of enhanced diffusion decreases and the viscosity change is mainly due to clustering. Although, clustering induced viscosity changes can also be observed in passive suspensions by, for instance, tuning the pH or temperature, one important distinction lies in the mechanism. In case of a passive suspension, the inter-particle interactions can lead to a low energy state, while here energy is actively dissipated to maintain the clustered state.

Since the base viscosity of the passive suspension can be tuned by increasing the particle density of the passive (fumed silica) component of the suspension, or the particle density of the active titania colloids, the system can be extended to show reversible changes in different viscosity regimes, depending on the desired applications. Further, as the powders are readily available at potentially kilogram quantities, we show that active chemical motors can be used at large scales, which opens up new possibilities in engineering applications of chemical motors and in forming novel active materials.

**Experimental Section**

**Colloids:** TiO₂ colloids were obtained from US Research Nano-Materials Inc., fumed silica (Aerosil 150) from Evonik, and Tempol from Sigma Aldrich.

**Microscopy:** All images were captured with a Zeiss Axio-Observer inverted microscope. The microscope images were captured using a 40 × 0.75 NA objective. A UV light emitting diode served as the light source for TiO₂ excitation. To capture the image stack, the focal plane was electronically adjusted and scanned.

**Bulk Rheology:** Bulk rheology measurements were performed in a HAAKE MARS III rheometer. A 35 mm parallel plate geometry with a 100 μm gap was used for all the measurements. The bottom plate was made of glass (1 mm thick) to allow for UV illumination. Four UV (365 nm) LEDs with an area of 6.3 × 6.3 mm and an output optical power of 5 W were mounted on a custom-made, water-cooled aluminum plate and arranged to provide uniform illumination on the sample. To minimize radiant heating from the LEDs, air-cooling was directed at the underside of the rheometer glass window. All rheological measurements were conducted in a custom-made humidity chamber to minimize evaporative losses during measurements.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

D.S. and P.F. acknowledge funding from the Baden-Württemberg Stiftung.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

active materials, bulk scale active colloids, chemical nanomotors, light-driven colloids, optically tunable soft matter

Received: November 14, 2018
Revised: December 21, 2018
Published online: January 30, 2019


