Demonstration

Colloidal Tornadoes in a Vial under Gravitational Sedimentation

Jianrui Zhang, Markus Antonietti, and Baris Kumru*

Cite This: *J. Chem. Educ.* 2021, 98, 1347−1351

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Collective motion in living matter is highly intriguing but can also be observed in charged colloidal systems. Collective motion observed in colloidal systems requires extensive material synthesis, external stimuli, and advanced characterization methods that might be highly costly to be employed for teaching. Besides that, colloidal systems can inherently possess dynamic movements. Generally, colloidal sedimentation is pictured as a linear movement, but under certain conditions autonomously activated sedimentation can be attained. In this demonstration, a simple formation of colloidal tornadoes will be explored by gravitational force as the sole stimulus. This demonstration is ideal for the general public for colloid chemistry learning, and these findings can be coupled to colloidal stability lectures.

Colloidal Tornadoes by Gravitational Sedimentation

KEYWORDS: *General Public, Public Understanding/Outreach, Multimedia-Based Learning, Colloids, Noncovalent Interactions*
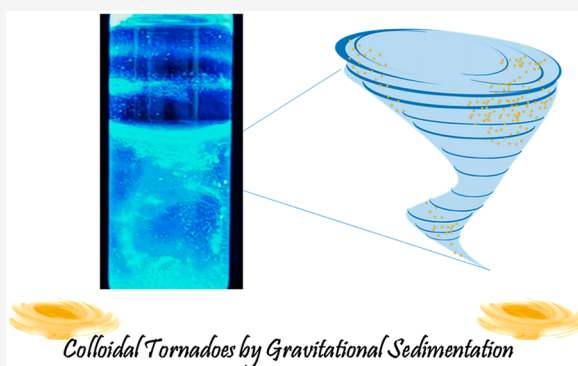
Organized motion is one of the main indicators to identify life. However, when nature is probed carefully, complex movements are observed also in dead matter, and a pattern is observed that is known as "collective motion".[1] In animal groups (as well as bacteriae[2]), the motion of one individual is strictly determined by the others, i.e., coupling is stronger than individuality, and decision making to reach a consensus about the timing (e.g., start) and the spatial direction/destination of the collective movement is complex.[3] Hierarchical collective motion can be contemplated in herds (e.g., zebras[4] or macaques[5]), where a single leader guides the whole community by assuring dominance.[6] On the other side, flock or swarm formation in fishes,[7] birds,[8] and insects[9] follows the concept of "common decision by the group".[1] The evolution of forming such dynamic structures obviously provided beneficial conditions for protection and hunting, yet the response of individuals to form almost autonomous group movement is still a mystery.[6]

Teaching colloid chemistry has been a long quest, and it was one of the major interests in the 1960s, as evidenced by the intensity of the publications.[10,11] In 1980, Sarquis prepared an overview report on colloidal systems and provided a brief summary even for nonexperts.[12] The tradition is now combined with technology, and widespread teaching of colloid chemistry basics is still desired by interactive means.[13,14] It is here very helpful that living systems can be simplified down to the nanomicroscale, namely, to colloidal systems that are made up of nonbiological matter.[15] This concept is highly related to colloidal stability and DLVO theory (named after the scientists Derjaguin, Landau, Verwey, and Overbeek), which allows the interplay of the forces experienced by a dispersion in relation to surface charge, temperature, and dielectric constant. Active

group-forming colloids reduce complexity to dispersion conditions and outer stimuli/forces, and it has been stated that the physical rules of colloidal and animal swarms are similar, so that tracking the motion of colloidal systems can help to set the base energetics and coupling rules underlying the "collective motion" in living systems.[15] Colloidal motions are generally activated by external stimuli such as heat,[16] light,[17] and electric field,[18] whereas special material morphologies and properties are needed to conduct the motion (e.g., Janus particles, which possess two different characters on the same particle, via either surface properties or being made of different elements; the name "Janus" arises from Roman mythology, in which Janus was a mythological god with two different faces).[19,20] Besides the importance of the movement of a single material (e.g., microswimmers), particle–particle interaction augments collective behavior to colloidal systems.[21]

Graphitic carbon nitride (g-CN) is a basic metal-free polymeric semiconductor that is typically utilized as a heterogeneous photocatalyst for a variety of applications through a visible-light-induced photoredox cycle.[22−26] The synthesis of g-CN relies on thermal condensation of nitrogen-rich monomers (e.g., urea and melamine), resulting in a hydrophobic core composed of tri-s-triazine units and hydrophilic noncondensed edges with a negative overall
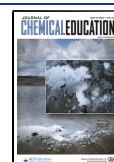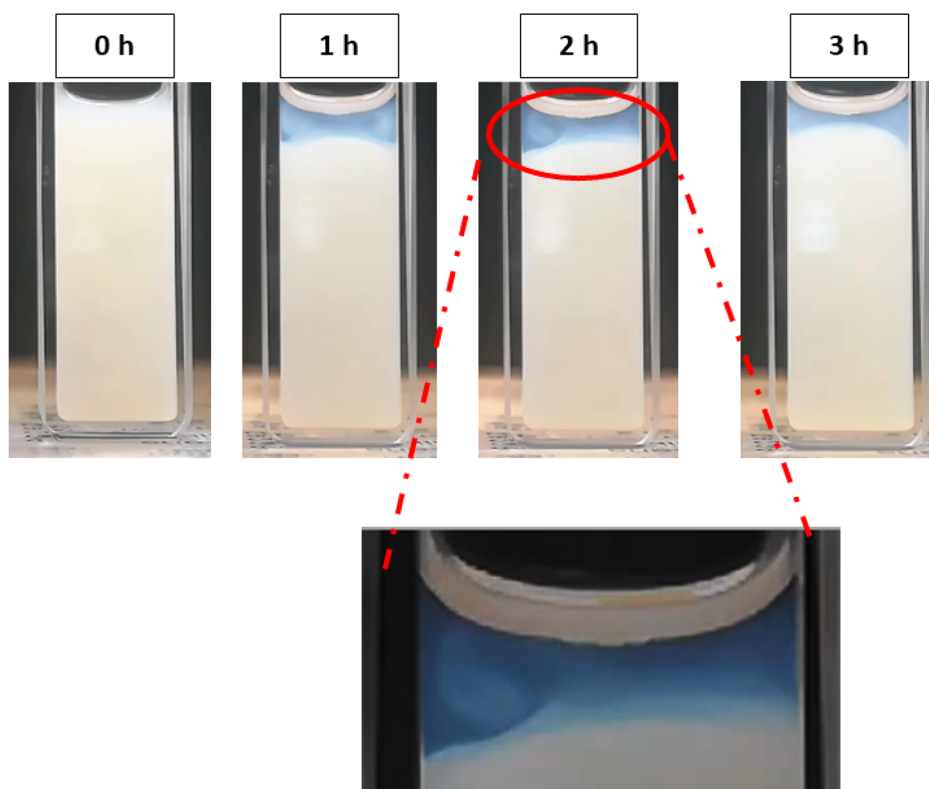
Figure 1. Snapshots from g-CN acetone dispersion (0.05 wt %) and formation of clouds on the top of the cuvette.

surface charge.[27] g-CN represents a class of materials that can be obtained by presynthetic (through synthetic pathways such as monomer treatment[28,29] and synthesis temperature[30,31]) or postsynthetic modifications (metal deposition,[32] surface modification[33,34]). In general, it is challenging to make colloidally stable g-CN dispersions (usually, attractive π interactions and hydrogen bonding dominate over repulsive forces).[35] Nevertheless, once formed, many novel applications are accessible, e.g., Pickering emulsions[36−38] and hybrid formation.[39,40]

In this demonstration, the interplay of attraction and repulsion in g-CN dispersions to generate dynamically coupled colloidal states under gravitational sedimentation conditions will be visualized. Additionally, the concept of a secondary minimum in DLVO theory and its tunability will be exhibited. The resulting dynamic conditions will be monitored by a video recording.

EXPERIMENTAL OVERVIEW

For the experiment, one requires a sonic bath, capped vials or a quartz cuvette, water, acetone, and carbon nitride. As carbon nitride represents a family of materials that vary by the sheet size and surface charge (from a colloid chemistry perspective), here carbon nitride synthesis from the condensation of a cyanuric acid−melamine supramolecular complex precursor was employed. The synthesis of carbon nitride requires 1.3 g of cyanuric acid and 1.8 g of melamine mixed in 50 mL of distilled water overnight. After filtration and drying at 50 °C overnight, the white complex is placed in a capped aluminum crucible, which is placed in a nitrogen-protected oven at 550 °C for 4 h (4 h to reach 550 °C, and another 4 h at 550 °C; the sample remains inside until the oven reaches room temperature). The resulting yellow powder is called g-CN.

Alternatively, g-CN can be purchased commercially, but that might influence the experimental conditions described here.

Specific masses of g-CN corresponding to concentrations of 0.05, 0.2, or 0.5 wt % are placed in water (3 mL) as well as acetone (3 mL) and sonicated in a sonic bath for 30 min to obtain colloidal suspensions, and then the vials or cuvettes are first allowed to rest for 6 h only for the sedimentation of larger sheets. Then the capped vials are placed in front of a recording source (camera recording or automatic imaging each 10 s, with the images later compiled into a video) and monitored over 6 h (after 6 h of sedimentation) at room temperature (23.5 °C was measured in the lab). It is important to keep the system at room temperature, as changes in temperature significantly influence the colloidal stability (the current demonstration was recorded at 23.5 °C). Another note is that the vials or cuvettes must be capped tightly in order to avoid solvent-evaporation-induced movements.

HAZARDS

Experiments must be performed with a lab coat, gloves, and safety goggles. Acetone must be handled under a fume hood. If g-CN is synthesized, the oven should be placed in a fume hood, and the high temperature of the oven and its surroundings must be minded.

RESULTS AND DISCUSSION

Brownian motion is the elemental dynamic process in colloidal systems,[41] but random collisions of particles will not set a base for collective movement. That is why here the focus is on particles with sufficient long-range repulsion to align trajectories long before potential collisions.

All colloidal dispersions experience gravitational force, which results in sedimentation.[41] In electric double layer systems,
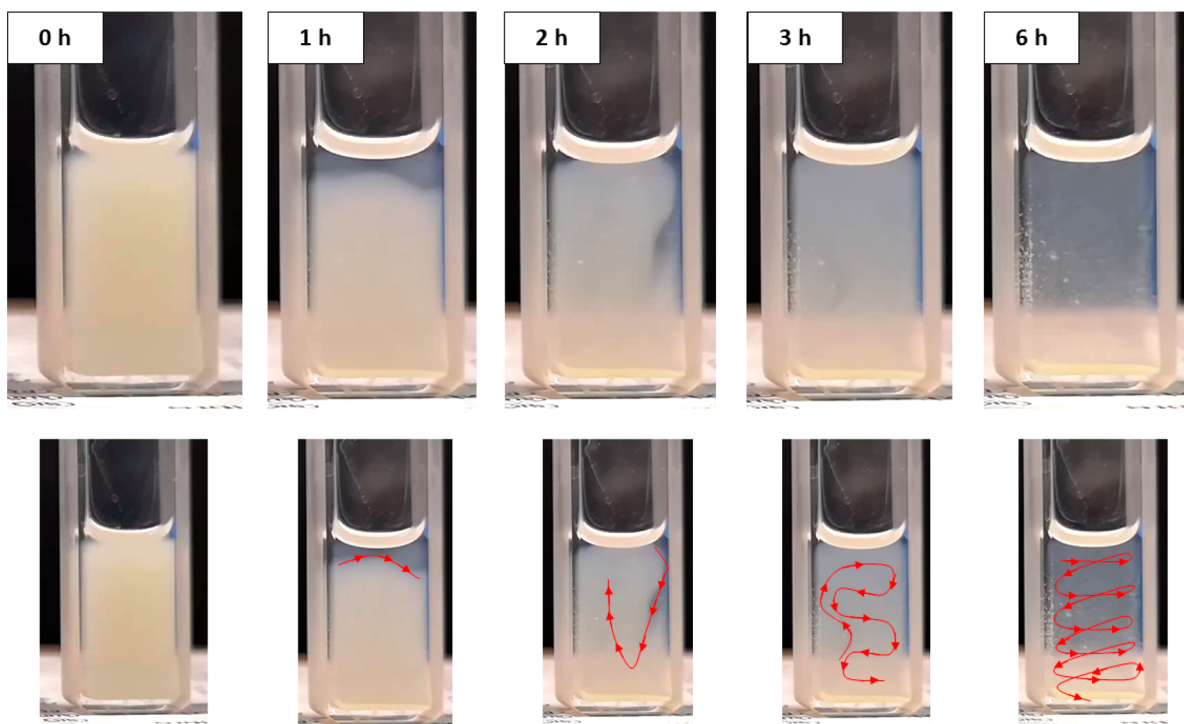
Figure 2. Snapshots from a g-CN acetone dispersion (0.2 wt %) and formation of tornadoes in the cuvette (red arrows are employed to visualize the colloidal movement pathway).

Scheme 1. Diagram of the Colloidal Stability and Two-Phase Regions and Their Relation to DLVO Potentials
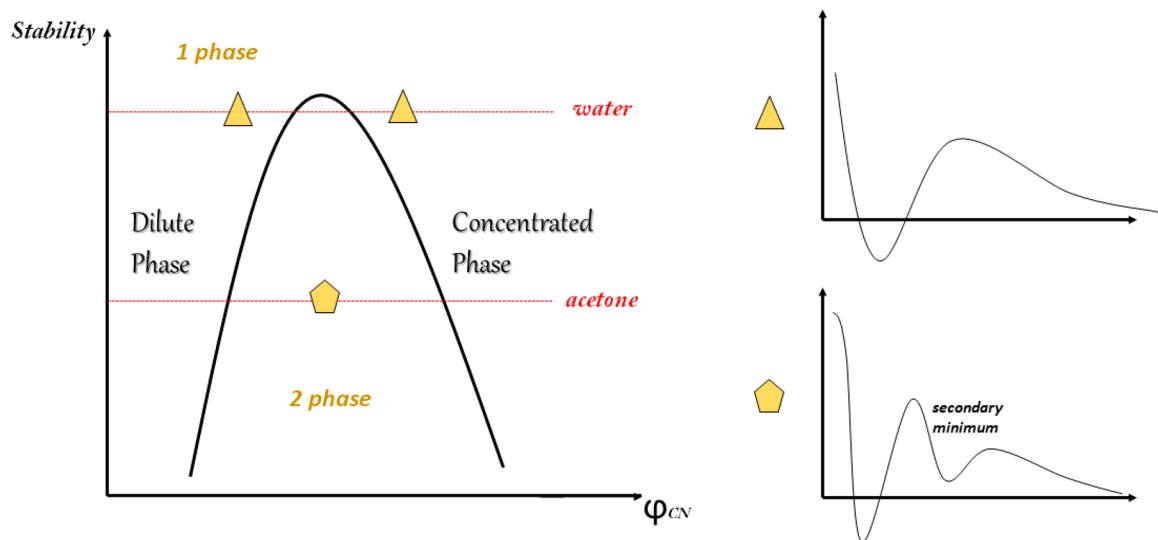
sedimentation is not prohibited but starts to be coupled with each other, thus creating larger systems with higher hydrodynamic drag. The suspending medium has an effect on such colloidal dynamics[42] by means of ion dissociation, effective charge, and then also the dielectric constant as well as by the density difference driving the sedimentation.

In the first sample of g-CN dispersion in acetone (0.05 wt %), the dynamics of colloidal systems is observed (Supporting Video 1). For the acetone dispersion, macroscopic vortex (cyclone) formation was observed at the top layer (Figure 1). When particle-rich fluid phase sediments, it forms an eddy force that pushes the particle-poor fluid phase back to the dispersion, indicating that the solvent is tightly coupled to the particles. This is beyond any traditional sedimentation models

that presume a stationary solvent phase. As there is still repulsion of g-CN in acetone, the sedimenting particle-rich dense fluid phase on average moves to the bottom but does not compact to a solid particle–particle contact layer. The dispersion is biphasic, with two different particle concentrations and the dense phase forming clouds that try to sediment. Here the incompressibility of the solvent creates a countermovement of a phase with a low density of particles, and the flux and counterflux stabilize into an eddy, a dynamic structure. Both the dilute phase and dense phase can be observed at the end of the experiment, one as the only slightly turbid overlayer and the other as a fluffy liquid sediment (Figure 1, 3 h cell).

The sediment can easily be shaken up and dispersed, and the experiment can start again. In this case, large particles will sediment right away because gentle mixing by hand does not provide a sufficient force (i.e., sonication) to temporarily disperse larger sheets, and thus, 6 h of waiting will not be necessary. Such observations highlight that the sedimentation and dispersion are dynamic and reversible. It should be noted that the secondary DLVO minimum could be determined by the concentration of the lower phase, while such a potential automatically comes with liquid−liquid phase demixing in the Gibbs phase diagram.

Increasing the g-CN concentration in the acetone dispersion, thereby increasing the depth within the biphasic region, has a significant effect on the macroscopic dynamics (Figure 2 and Supporting Video 2). A colloidal tornado was formed in this case, accompanied by a higher amount of high-concentration g-CN phase in acetone. In this case, the clouds are more extended, and the force exerted by the particle-rich dense phase (dispersed phase) forming couples throughout the cuvette into one tornado-like eddy with relatively high energy.

All of these experiments suggest that dispersibility of the particles in a specific solvent is a prerequisite and that having a two-liquid-phase colloidal system is the main factor driving the intensity and shape of the dynamic movement (Scheme 1).

As a proof of concept, the solvent can be changed to water. From the scheme and general knowledge, g-CN has better stability in aqueous dispersions, and thus, the two-phase region is strictly limited. One can perform similar experiments with 0.05 or 0.2 wt % g-CN in water, but no movement will be observed. Increasing the concentration to 0.5 wt % grants access to a two-phase region, and tornado formation is clearly observable (Supporting Video 3). As stated before, the reversibility of the sedimentation−dispersion dynamics was exhibited by shaking the vial, and tornado formation was visible as expected (Supporting Video 3). These simple experiments allow visualization of the effect of the solvent and concentration on the colloidal stability and how the active colloid regimes can be accessed. Depending on the polarity of organic solvents and the concentration, one can play with the DLVO potential to form partial attraction between the particles, and establishing the secondary minimum of the interaction potential allows the formation of two coexisting liquid phases. The denser phase is subjected to gravitational sedimentation, while the electrostatic coupling forces the system to sediment as a "swarm", and macroscopic collective movements can be visualized. Despite the current understanding of sedimentation, which postulates that the particles move only toward the bottom while the lighter phase streams in the opposite direction, long-range-coupled colloids possess an entirely different behavior. The behavior is similar to that of rain clouds, where the parallel movement of raindrops carries the air with them, with macroscopic wind counterstreams on the outside of the clouds replacing the pulled-away medium. The resulting circulation can move part of the dispersion for a number of cycles around and can be active for up to 6 h.

The main learning outcome of this demonstration is an introduction to colloidal forces, DLVO theory, and colloidal stability. One can grasp information about the complexity of the colloidal systems, and video demonstrations provide active conditions granted solely by gravitational sedimentation. This demonstration has been presented at a research institute for a crowd with a diverse scientific background (mostly with a Ph.D. degree), and around 60% of the attendees were interested in further discussions.

■ SUMMARY

Depending on the dispersion medium and concentration, one can dive different depths into the two-phase region. Small jumps first create only ripples and small eddy waves in the top layer, while deeper jumps and the corresponding higher driving forces create the described rain cloud circulations. Finally, after deep jumps into the two-phase region, tornado formation takes place as the sedimentation of the particle-rich higher-density phase creates one dynamically coupled entity extending over the whole cuvette. This simple visualization of the DLVO diagram and how simple solvent and concentration tuning affect the formation of active systems will grasp the interest of students and the general public toward colloid chemistry. Furthermore, the simplicity of this experiment, without the need for toxic/expensive/hazardous chemicals and employing a multimedia tool (video) for characterization, renders it suitable to be conducted all over the world.

■ ASSOCIATED CONTENT

si Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.0c01507.

    Supporting Video 1 (MP4)
    Supporting Video 2 (MP4)
    Supporting Video 3 (MP4)

■ AUTHOR INFORMATION

Corresponding Author

    Baris Kumru − *Max Planck Institute of Colloids and Interfaces, 14424 Potsdam, Germany;* ⓘ orcid.org/0000-0002-1203-4019; Email: baris.kumru@mpikg.mpg.de

Authors

    Jianrui Zhang − *Max Planck Institute of Colloids and Interfaces, 14424 Potsdam, Germany*
    Markus Antonietti − *Max Planck Institute of Colloids and Interfaces, 14424 Potsdam, Germany*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.jchemed.0c01507

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Vicsek, T.; Zafeiris, A. Collective motion. *Phys. Rep.* **2012**, *517* (3−4), 71−140.

(2) Sokolov, A.; Aranson, I. S.; Kessler, J. O.; Goldstein, R. E. Concentration dependence of the collective dynamics of swimming bacteria. *Phys. Rev. Lett.* **2007**, *98* (15), 158102.

(3) Conradt, L.; Roper, T. J. Deciding group movements: Where and when to go. *Behav. Processes* **2010**, *84* (3), 675−677.

(4) Fischhoff, I. R.; Sundaresan, S. R.; Cordingley, J.; Larkin, H. M.; Sellier, M.-J.; Rubenstein, D. I. Social relationships and reproductive

state influence leadership roles in movements of plains zebra, Equus burchellii. *Anim. Behav.* **2007**, *73*, 825−831.

(5) Sueur, C.; Petit, O. Organization of group members at departure is driven by social structure in macaca. *Int. J. Primatol.* **2008**, *29*, 1085−1098.

(6) Petit, O.; Bon, R. Decision-making processes: The case of collective movements. *Behav. Processes* **2010**, *84*, 635−647.

(7) Ward, A. J. W.; Sumpter, D. T. J.; Couzin, I. D.; Hart, P. J. B.; Krause, J. Quorum decision-making facilitates information transfer in fish shoals. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105* (19), 6948−6953.

(8) Bajec, I. L.; Heppner, F. H. Organized flight in birds. *Anim. Behav.* **2009**, *78*, 777−789.

(9) Buhl, J.; Sumpter, D. J. T.; Couzin, I. D.; Hale, J. J.; Despland, E.; Miller, E. R.; Simpson, S. J. From disorder to order in marching locusts. *Science* **2006**, *312*, 1402−1406.

(10) Slabaugh, W. H. The teaching of colloid and surface chemistry. Symposium introduction. *J. Chem. Educ.* **1962**, *39* (4), 166.

(11) Zettlemoyer, A. C. Colloid and surface chemistry in the physical chemistry course. *J. Chem. Educ.* **1962**, *39* (4), 180−183.

(12) Sarquis, J. Colloidal systems. *J. Chem. Educ.* **1980**, *57* (8), 602−605.

(13) Yin, D.; Chen, J.; Gu, B.; Geng, W. Investigating the Phase Inversion of Pickering Emulsions: An Experiment To Explore Colloid and Interface Chemistry Concepts. *J. Chem. Educ.* **2018**, *95* (4), 662−665.

(14) Radzikowski, J. L.; Delmas, L. C.; Spivey, A. C.; Youssef, J.; Kneebone, R. The Chemical Kitchen: Toward Remote Delivery of an Interdisciplinary Practical Course. *J. Chem. Educ.* **2021**, DOI: 10.1021/acs.jchemed.0c01047.

(15) Zhang, J.; Luijten, E.; Grzybowski, B. A.; Granick, S. Active colloids with collective mobility status and research opportunities. *Chem. Soc. Rev.* **2017**, *46*, 5551−5569.

(16) Palacci, J.; Cottin-Bizonne, C.; Ybert, C.; Bocquet, L. Sedimentation and Effective Temperature of Active Colloidal Suspensions. *Phys. Rev. Lett.* **2010**, *105* (8), 088304.

(17) Ji, F.; Jin, D.; Wang, B.; Zhang, L. Light-Driven Hovering of a Magnetic Microswarm in Fluid. *ACS Nano* **2020**, *14* (6), 6990−6998.

(18) Ma, F.; Yang, X.; Zhao, H.; Wu, N. Inducing Propulsion of Colloidal Dimers by Breaking the Symmetryin Electrohydrodynamic Flow. *Phys. Rev. Lett.* **2015**, *115* (20), 208302.

(19) Yan, J.; Bloom, M.; Bae, S. C.; Luijten, E.; Granick, S. Linking synchronization to self-assembly using magnetic Janus colloids. *Nature* **2012**, *491*, 578−581.

(20) Wang, W.; Castro, L. A.; Hoyos, M.; Mallouk, T. E. Autonomous Motion of Metallic Microrods Propelled by Ultrasound. *ACS Nano* **2012**, *6* (7), 6122−6132.

(21) Zhang, J.; Yan, J.; Granick, S. Directed Self-Assembly Pathways of Active Colloidal Clusters. *Angew. Chem., Int. Ed.* **2016**, *55* (17), 5166−5169.

(22) Kuriki, R.; Sekizawa, K.; Ishitani, O.; Maeda, K. Visible-Light-Driven CO2 Reduction with Carbon Nitride: Enhancing the Activity of Ruthenium. *Angew. Chem., Int. Ed.* **2015**, *54* (8), 2406−2409.

(23) Karjule, N.; Phatake, R.; Volokh, M.; Hod, I.; Shalom, M. Solution-Processable Carbon Nitride Polymers for Photoelectrochemical Applications. *Small Methods* **2019**, *3* (12), 1900401.

(24) Yang, Z.; Zhang, Y.; Schnepp, Z. Soft and hard templating of graphitic carbon nitride. *J. Mater. Chem. A* **2015**, *3* (27), 14081−14092.

(25) Thurston, J. H.; Hunter, N. M.; Cornell, K. A. Preparation and characterization of photoactive antimicrobial graphitic carbon nitride (g-C3N4) films. *RSC Adv.* **2016**, *6* (48), 42240−42248.

(26) Cao, Q.; Kumru, B.; Antonietti, M.; Schmidt, B. V. Grafting polymers onto carbon nitride via visible-light-induced photofunctionalization. *Macromolecules* **2019**, *52* (13), 4989−4996.

(27) Ong, W.-J.; Tan, L.-L.; Ng, Y. H.; Yong, S.-T.; Chai, S.-P. Graphitic carbon nitride (g-C3N4)-based photocatalysts for artificial photosynthesis and environmental remediation: are we a step closer to achieving sustainability? *Chem. Rev.* **2016**, *116* (12), 7159−7329.

(28) Vu, N.-N.; Nguyen, C.-C.; Kaliaguine, S.; Do, T.-O. Synthesis of g-C₃N₄ Nanosheets by Using a Highly Condensed Lamellar Crystalline Melamine−Cyanuric Acid Supramolecular Complex for Enhanced Solar Hydrogen Generation. *ChemSusChem* **2019**, *12*, 291−302.

(29) Barrio, J.; Shalom, M. Rational Design of Carbon Nitride Materials by Supramolecular Preorganization of Monomers. *ChemCatChem* **2018**, *10* (24), 5573−5586.

(30) Zhou, J.; Yang, Y.; Zhang, C.-Y. A low-temperature solid-phase method to synthesize highly fluorescent carbon nitride dots with tunable emission. *Chem. Commun.* **2013**, *49*, 8605−8607.

(31) Das, D.; Banerjee, D.; Pahari, D.; Ghorai, U. K.; Sarkar, S.; Das, N. S.; Chattopadhyay, K. K. Defect induced tuning of photoluminescence property in graphitic carbon nitride nanosheets through synthesis conditions. *J. Lumin.* **2017**, *185*, 155−165.

(32) Shiraishi, Y.; Kofuji, Y.; Kanazawa, S.; Sakamoto, H.; Ichikawa, S.; Tanaka, S.; Hirai, T. Platinum nanoparticles strongly associated with graphitic carbon nitride as efficient co-catalysts for photocatalytic hydrogen evolution under visible light. *Chem. Commun.* **2014**, *50* (96), 15255−15258.

(33) Zhang, G.; Lan, Z.-A.; Wang, X. Surface engineering of graphitic carbon nitride polymers with cocatalysts for photocatalytic overall water splitting. *Chem. Sci.* **2017**, *8* (8), 5261−5274.

(34) Kumru, B.; Molinari, V.; Hilgart, M.; Rummel, F.; Schaeffler, M.; Schmidt, B. V. K. J. Polymer Grafted Graphitic Carbon Nitride as Precursors for Reinforced Lubricant Hydrogels. *Polym. Chem.* **2019**, *10*, 3647−3656.

(35) Kumru, B.; Antonietti, M. Colloidal properties of the metal-free semiconductor graphitic carbon nitride. *Adv. Colloid Interface Sci.* **2020**, *283*, 102229.

(36) Luo, Y.; Yang, Y.; Cui, Q.; Peng, R.; Liu, R.; Cao, Q.; Li, L. Fluorescent Nanoparticles Synthesized by Carbon-Nitride-Stabilized Pickering Emulsion Polymerization for Targeted Cancer Cell Imaging. *ACS Appl. Bio Mater.* **2019**, *2* (11), 5127−5135.

(37) Han, C.; Cui, Q.; Meng, P.; Waclawik, E. R.; Yang, H.; Xu, J. Direct Observation of Carbon Nitride-Stabilized Pickering Emulsions. *Langmuir* **2018**, *34* (34), 10135−10143.

(38) Cao, Q.; Heil, T.; Kumru, B.; Antonietti, M.; Schmidt, B. V. K. J. Visible-light induced emulsion photopolymerization with carbon nitride as a stabilizer and photoinitiator. *Polym. Chem.* **2019**, *10*, 5315−5323.

(39) Shi, L.; Wang, T.; Zhang, H.; Chang, K.; Ye, J. Electrostatic Self-Assembly of Nanosized Carbon Nitride Nanosheet onto a Zirconium Metal−Organic Framework for Enhanced Photocatalytic CO₂ Reduction. *Adv. Funct. Mater.* **2015**, *25* (33), 5360−5367.

(40) Yandrapalli, N.; Robinson, T.; Antonietti, M.; Kumru, B. Graphitic Carbon Nitride Stabilizers Meet Microfluidics: From Stable Emulsions to Photoinduced Synthesis of Hollow Polymer Spheres. *Small* **2020**, *16* (32), 2001180.

(41) Yuan, Y.; Tasinkevych, M.; Smalyukh, I. I. Colloidal interactions and unusual crystallization versus de-mixing of elastic multipoles formed by gold mesoflowers. *Nat. Commun.* **2020**, *11*, 188.

(42) Ruckenstein, E.; Rao, I. V. Effect of solvent on the stability of mixtures of sterically stabilized dispersions and free polymers. *Colloids Surf.* **1986**, *17* (3), 185−205.