Dielectrophoretic Assembly of Metallodielectric Janus Particles in AC Electric Fields

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Received May 17, 2008. Revised Manuscript Received August 30, 2008

“Janus” particles with two hemispheres of different polarizability or charge demonstrate a multitude of interesting effects in external electric fields. We reported earlier how particles with one metallic hemisphere and one dielectric hemisphere self-propel in low-frequency alternating current (AC) electric fields. Here, we demonstrate the assembly of such Janus particles driven by AC electric fields at frequencies above 10 kHz. We investigated the relation between field-induced dielectrophoretic force, field distribution, and structure of the assemblies. The phase space for electric field intensity and frequency was explored for particle concentrations large enough to form a monolayer on a glass surface between two gold electrodes. A rich variety of metallodielectric particle structures and dynamics were uncovered, which are very different from those obtained from directed assembly of plain dielectric or plain conductive particles under the action of fields of similar frequency and intensity. The metallodielectric particles assemble into new types of chain structures, where the metallized halves of neighboring particles align into lanes along the direction of the electric field, while the dielectric halves face in alternating direction. The staggered chains may assemble in various orientations to form different types of two-dimensional metallodielectric crystals. The experimental results on the formation of staggered chains are interpreted by means of numerical simulations of the electric energy of the system. The assembly of Janus metallodielectric particles may find applications in liquid-borne microcircuits and materials with directional electric and heat transfer.

1. Introduction

Isotropic spherical colloids, typically made of silica or latex, have been the focus of particle assembly for more than 50 years. There is growing recognition that anisotropic particles can be used to engineer the assembly of targeted structures. “Janus” particles, named by Casagrande and de Gennes after the Roman mythology god (who possessed two faces), are one such class of anisotropic colloids. Janus particles have surface coverage or “patchiness” yielding surface properties that are physically or chemically different. Various techniques have been formulated recently to synthesize Janus particles, as they are an interesting object of study and can find potential applications in novel materials.

Anisotropic particles with two hemispheres of different polarizability and/or conductance have been produced by thermal evaporation or gold sputtering. Molecular simulations have been used to investigate the assembly of functionally anisotropic building blocks. However, few experimental studies report how such Janus particles assemble or respond to external fields.

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Hong et al. have assembled spherical particles with opposite electric charge on the hemispheres in a system where the particle diameter exceeds the electrostatic screening length. These particles formed clusters rather than strings, and Monte Carlo simulations have been performed to analyze the experimental results. Behrend et al. have coated magnetic and nonmagnetic particles with metal and tracked the orientation and rotation of these particles in magnetic fields to calculate the torque acting on the particles. Takei et al. have investigated the orientation of anisotropic particles in low frequency (0.1–1 Hz) electric fields after chemically modifying the gold hemisphere with charged thiols. The orientation of these dipolar particles in an electric field depends on the pH, which controls the charge of the functionalized hemispheres. Crowley et al. have determined the dipole response of a “gyricon” ball (∼100 μm diameter), which consists of two hemispheres of different colors and different electrical properties. These gyricon balls (with white- and black-colored halves) can be rotated when immersed in a liquid and exposed to a uniform electric field, which has application in “electric paper” electronic displays.

Externally applied electric fields allow the precise tuning of forces exerted on the particles and the fluid medium by the field. Dielectrophoresis (DEP) is a force that emerges upon application

of an electric field (direct current, DC, or alternating current, AC) to a suspension of particles. The application of an electric field across a suspension of isotropic colloidal particles leads to their polarization. The DEP force arises when the particles’ induced dipoles interact with a nonuniform electric field leading to particle movement. The particles are either attracted (positive DEP) to the region of maximum field intensity or repelled (negative DEP) from it, depending on the effective particle polarization relative to the media. The particle “chainging” force is described as a result of the attraction of the induced dipoles within the particles. The chaining force acting between particles of the same type is always positive and attractive.

AC electric fields can be used to manipulate many types of colloidal particles in different media by simply adjusting AC electric field parameters (magnitude, frequency, wave shape, wave symmetry, and phase). Our research group has used DEP for the formation of colloidal crystals, linear aggregates of nanoparticles, and carbon nanotubes (CNTs). Our research group has used DEP for the formation of colloidal crystals, linear aggregates of nanoparticles, and carbon nanotubes (CNTs). We have used simulations to describe the assembly and calculate the electric field distribution around pairs of dielectric particles and pairs of metallic particles subject to an AC electric field between two coplanar electrodes. We report here new assembly effects and patterns driven by AC electric fields applied to suspensions of Janus metallodielectric particles. In our previous work, we showed that the application of low frequency (∼10 kHz) AC electric fields to suspensions of micrometer-sized Janus particles with one dielectric hemisphere and one conductive hemisphere resulted in unbalanced liquid flows and nonlinear, induced-charge electrophoretic (ICEP) motion of the particles. The particles moved perpendicular to the uniform applied electric field, with their polystyrene hemisphere forward. Here, we report the dielectrophoretic assembly of micrometer-sized metallodielectric Janus particles suspended in water, subject to high frequency (> 10 kHz) AC electric fields. We first describe the technique for Janus particle preparation, the experimental setup, and the procedures for numerical simulations. The experimental data are presented and summarized in the parameter space for electric field intensity and field frequency. The metallodielectric particle concentrations were large enough to form a monolayer (on the glass surface), and a rich variety of structures was uncovered. Results from two-dimensional (2D) numerical simulations of the electric energy of the system are correlated with the experimental results.

2. Experimental Procedures

Materials. Deionized water with a resistivity of 18.2 MΩ cm was obtained from a MilliQ Plus water purification system. Surfactant-free polystyrene latex microspheres (diameter, D = 40 and 5.7 μm) stabilized by sulfate groups were purchased as aqueous dispersions from Interfacial Dynamics Corp. (OR). Nonionic surfactant polyoxyethylene(20)sorbitan (Tween-20) was purchased from Acros Organics (NJ). Ethanol and Teflon tape were purchased from Fisher Scientific (PA).

Janus Metallodielectric Particle Preparation. The metallodielectric particles used in the experiments were prepared by partially coating the polystyrene microspheres with a conductive layer of gold on one hemisphere of the particles. The polystyrene particles were initially concentrated by centrifuging at ∼2000g for 10 min and were washed with ultrapure Milli-Q water. A convective assembly method that we had engineered previously was used to deposit particle submonolayers on precleaned glass microscope slides (Fisher Scientific, PA). The dried particle submonolayers were coated with 10 nm of chromium followed by 20 nm of gold in a metal evaporator. The chromium layer was deposited to ensure that gold adheres to the exposed particle surface. The “Janus” particles formed (Figure 1b) were then dispersed in Milli-Q water by spraying the glass slides coated with metal-coated particles with a 1:3 (v/v) ethanol/Milli-Q water solution to flush the particles using a 30 μL syringe fitted with a 18G1/2 needle. The remaining particles on the glass slides were removed by mild sonication (for less than 20 s). Nonionic surfactant Tween-20 (∼0.1 wt %) was added to the suspensions, and the particles were washed with Milli-Q water to remove the ethanol. Addition of the nonionic surfactant prevented the particles from aggregating. High concentration suspensions of Janus particles (∼7–12% solids) in small volumes (∼50–100 μL) were prepared by centrifugation. The concentration of particles in suspension was calculated based on the number of particles necessary to form a close-packed monolayer on the bottom surface of the experimental cell (Figure 1a).

Experimental Setup. The experimental cell (Figure 1a) was constructed from a glass slide onto which two coplanar gold electrodes (3 mm interelectrode gap) were deposited by evaporating 10 nm of chromium followed by 100 nm of gold. A liquid blocker pen was used to create a “corral” between the electrodes surrounded by a hydrophobic ring. A 2–3 μL droplet suspension of the Janus particles was placed within this area onto the bottom microscope glass in contact with both electrodes. A microscope glass coverslip was placed directly on top of the particle suspension, forming a thin experimental...
the particle suspension. A 1 to 90 V and frequencies from 1 to 200 kHz was applied to (Burleigh, NY). An AC field (of square waveform) of voltage ranging at high and low frequencies were recorded using a Sony Cybershot digital CCD camera. Digital movies of the Janus particles’ behavior above using an Olympus BX-61 optical microscope (with 40× objective), and images were recorded using an Olympus DP-70 camera. Digital movies of the Janus particles’ behavior at high and low frequencies were recorded using a Sony Cybershot DSC-V1 camera fitted to the eyepiece of the microscope.

The alternating electric field within the experimental cell was produced by an Agilent 33120A 15 MHz function generator (Agilent Technologies, CO) connected to a RG-91 ramp generator/amplifier (Burleigh, NY). An AC field (of square waveform) of voltage ranging from 1 to 90 V and frequencies from 1 to 200 kHz was applied to the particle suspension. A 1 µF capacitor was included in the circuit to filter any direct current component of the signal. The voltage applied in the chamber was measured with a digital multimeter (Instek, CA). A master switch allowed starting and stopping the process.

**Numerical Simulation.** During one-half cycle of the applied AC field, the electric field distribution and electric energy distribution around the Janus particles inside the experimental cell were simulated by 2D electrostatic calculations using the FEMLAB multiphysics modeling package (COMSOL, Burlington, MA). The geometry of the system with metallodielectric particles (simulated with diameter of 5 µm) and the 3 mm gap between the electrodes were specified, the solution space was triangulated into a conformal mesh and the mesh was refined at least four times. The solver was initialized to solve the Poisson equation for all elements to obtain the electric field intensity and electrical energy density within the cell. The subdomain integration function was used to calculate the electric energy of the entire 2D system. This function integrated the electric energy density over the area (since this was a 2D simulation) of the system after selecting all four of the subdomains. The calculations were repeated with more refined mesh sizes until the mesh was small enough for the final calculated values to vary by less than 0.05%.

**3. Experimental Results**

**Effect of AC Field Strength and Frequency.** A wide variety of novel structures were formed and diverse particle dynamics were observed when the voltage and frequency of the applied AC field were varied at Janus particle concentrations large enough to form a monolayer on the bottom substrate. The crystallization and electrohydrodynamic mobility thresholds for the anisotropic microparticles were explored by adjusting the parameters of the applied field: the Janus particles could be made to display electrophoretic and electrohydrodynamic mobility in the direction perpendicular to the electric field as demonstrated in previous work; form crystals of unique symmetries by confining staggered chains of Janus particles in a small area; or form more complex three-dimensional (3D) bundle structures. The staggered chains, 2D crystal structures, and 3D bundle structures disassembled once the electric field was turned off, proving that this process was reversible.

The different regions of the dynamic and structural behavior of particles within the space of field intensity and frequency are presented in Figure 2. The AC field-induced dielectrophoretic or electrohydrodynamic response of the metallodielectric microparticles in Milli-Q water depends strongly on the frequency of the applied field. At higher frequencies, the metallodielectric particles formed staggered chains, 2D metallodielectric crystals, and 3D bundles, whereas at lower frequencies the anisotropic particles formed regular chains and performed induced-charge electrophoretic (ICEP) motion in the direction perpendicular to the applied field direction. The transition from staggered chain structures formed at high AC field frequency to ICEP motion at low frequency is shown in the Supporting Information. The regions outlined in Figure 2 are reviewed in more detail and their structure is analyzed in the next subsections.

**Disordered Particles Region.** Below ~25 V cm⁻¹ over the whole range of frequencies (1–200 kHz), the Janus metallodielectric particles remained disordered and were randomly distributed on the surface of the bottom glass slide due to Brownian motion (Figure 2, bottom). Most of the Janus particles were observed to assume an orientation such that the dark, gold-coated hemisphere was facing up and the light, polystyrene hemisphere was facing down, in contact with the bottom glass surface of the experimental cell. This could result from differences in the interactions between the metallic/polymer halves of the particles and the glass bottom wall of the experimental cell; however, this effect is easily overridden by the much stronger field-induced interactions and orientation at higher field strengths.

**Induced Charge Electrophoresis (ICEP) Region.** Above fields of approximately 75 V cm⁻¹, ICEP motion resulted at AC frequencies of 1–40 kHz (Figure 2), whereby the metallodielectric Janus particles moved in directions perpendicular to the electric field with their polystyrene hemispheres facing forward in the direction of motion. Our previous report explains the physical phenomenon and characterizes this ICEP motion as a function of field strength and frequency, electrolyte concentration, and

![Figure 1.](image-url)
Briefly, the electric double layer on the gold-coated conductive hemisphere of the particle is more strongly polarized in the applied field, which drives a stronger induced-charge electro-osmosis (ICEO) slip than that on the dielectric polystyrene side, resulting in ICEP motion in the direction of the uncoated side. Although we previously reported that ICEP motion decreases at about 12 kHz in cells of 60–80 µm heights, we found that ICEP motion persisted up to ~40 kHz at high field strengths in experimental cells of smaller heights (10–15 µm). The transition to the ICEP region from the 2D crystallization and 3D bundle region in Figure 2 was sensitive to the operating parameters. By slightly increasing the field strength, the stationary 2D crystals formed at low frequencies and lower field strengths could be forced to disassemble and perform ICEP motion, leading to “melting” of the crystals, which may be related to tangential double layer conductance. Also, by slightly decreasing the field frequency, the formed stationary 3D bundles at medium frequencies and medium field strengths could be made to disassemble and display ICEP motion. The particle chains tended to disassemble from the ends of the structure. Individual particles in 3D bundles or in staggered chains detached from the chain and began ICEP motion as the structure collapse proceeded inward from the ends (as displayed in the Supporting Information).

3D Bundles Region. The particles formed 3D bundles (top optical image of Figure 2, and Figure 4c) above ~75 V cm⁻¹ over the frequency range of 5–200 kHz. In the higher field strength, the particles in the 2D metallodielectric crystals packed more tightly. The particle chains stacked on top of each other up to the height of the experimental cell forming the 3D bundles (which might be nuclei for 3D crystals). Large void areas are observed between the 3D bundles. The higher DEP and particle chaining forces within the cell resulted in particle chains merging into the 3D bundles, increasing the bundles’ width and height. These bundles also tended to stretch toward each of the electrodes. Some of the particles were observed to rotate about their axes within the 3D bundles when higher field strengths were applied. Most of the particles in the 3D bundle optical images are observed with their dark, gold-coated hemispheres facing up.

Regular and Staggered Chains Region. The particles formed regular, straight chains parallel to the electric field direction similar to chains observed for plain latex particles in applied AC electric fields and staggered chains from 25 to ~40 V cm⁻¹ over the whole range of frequencies studied (1–200 kHz). At frequencies lower than ~10 kHz and low field strengths, the regular, parallel chains were oriented such that mostly the darker, gold-coated hemisphere of the particle was facing up (away from the bottom glass surface) as seen in the bottom left optical image of Figure

Figure 2. Dynamic and structural response of Janus particles to AC electric field intensity versus field frequency in a thin experimental cell. In the optical images, the gold-coated, conductive hemispheres appear dark and the bare, dielectric hemispheres appear light. The electric field direction is between the top and bottom of the optical images. The regions were established on the basis of 28 data points.

Figure 3. Optical micrographs of (a) staggered chains formed at lower concentration of Janus particles (5.7 µm diameter) in an AC field of 56 V cm⁻¹ at 40 kHz and (b) concentrated staggered chains formed with a particle concentration enough to form a monolayer in an AC field of 27 V cm⁻¹ at 40 kHz. The gold-coated, conductive hemispheres appear dark and bare, and dielectric hemispheres appear light. The electric field direction is between the top and bottom of the images. The scale bars in (a) and (b) are 70 and 50 µm, respectively.

2. At frequencies above $\sim 10$ kHz, the Janus particles formed staggered chains (bottom right optical image of Figure 2, and Figure 3a). When the electric field in the cell was turned on, the particles first oriented so that the plane between their hemispheres (gold-coated, conductive hemisphere appearing dark and bare, dielectric hemisphere appearing light) aligned in the direction of the electric field and subsequently formed chains. Within the staggered chain, the particles positioned themselves such that the polystyrene hemispheres of each particle were facing in alternating directions and only the gold-coated portions of the particles were in contact near the poles of the particle. The staggered chains were thus seen to have a dark gold line throughout the length of the chain aligned with the direction of the electric field.

When the electric field was turned off, both the straight and staggered chains came apart and the particles redispersed. The chain disassembly once the field was turned off could be attributed to both steric repulsion between the particles by the polyoxyethylene chains of the Tween 20 adsorbed on the surface of the particle and Brownian motion. The particles usually reoriented themselves so that their gold-coated hemispheres were facing up and the polystyrene hemisphere was in contact with the bottom glass substrate. This disassembly process contrasts with the aggregation of metallic gold nanoparticles induced by an AC electric field (within a cell similar to the one used here), where the assembled structures remained stable even after the voltage was turned off. The aggregation of these gold nanoparticles is irreversible due to the strong van der Waals forces acting on the nanoparticles. The disassembly process of metallodielectric Janus particles is similar to that of plain sulfate-stabilized polystyrene particles in AC electric fields, where the negatively charged sulfate groups on the plain polystyrene surface promote repulsion from overlapping electric double layers between the particles.

2D Crystallization Region. By further increasing the electric field intensity within the cell, we attempted to form two-dimensional lattices of staggered chains (Figure 3b). There is a narrow window for 2D metallodielectric crystal formation between $\sim 40$ and $75$ V cm$^{-1}$ across the range of frequencies studied, where lattices form due to dipolar attraction of contiguous chains. At low frequencies ($1 \sim 10$ kHz), 2D crystals formed with the gold-coated hemispheres of the particles facing up and the uncoated side facing the bottom glass substrate (Figure 2, middle-left optical image). From $10 \sim 200$ kHz, we observed formation of two types of crystals (Figure 2, middle optical images). The first particle lattice comprised narrow parallel metallic lanes throughout the crystal (Figure 4a). This lattice was formed when the applied higher voltage directed the assembly of staggered chains (formed in the lower-field region in Figure 2) into a close-packed lattice. Additionally, a second type of lattice appeared to possess broader metallic lanes due to the different positions of the approaching chains of particles with respect to each other. The chains forming this type of lattice were grouped together with the gold-coated hemispheres of each of the chains facing one another (Figure 4b). Within these two particle chain sets, the gold portion of each particle touched the gold portion of its neighboring four particles near the equator and the poles rather than just near the poles as in the first type of Janus crystal. The dielectric half of the particle was adjacent to the dielectric half of a particle from the next chain set. The first type of crystal lattice was observed more frequently and was larger in domain areas than the second type over the range of frequencies studied.

Characterization of Metallodielectric 2D Crystals. We further characterized the staggered chain and 2D crystallization regions using the orientational order and polarization parameters, which are commonly used to characterize dipolar liquid crystals. Similarly to liquid crystals, a specific orientation of the metallodielectric particles within the 2D crystalline lattices can be designated a specific orientation with regards to the plane between the metallic and dielectric halves of the particles. The orientation order parameter, $S$, can be expressed as the average

\[ S = \frac{1}{2} \left( \frac{3}{2} \cos^2 \theta - 1 \right) \]

where $\theta$ is the angle between the long axis of the particles and the direction of the electric field. The parameter $S$ varies from $-1/2$ (random orientation) to $1$ (perfect orientation).

Figure 4. Optical micrographs of (a) a crystal of staggered chains, (b) a crystal of two coexisting particle chain arrangements in an AC field of 125 kHz frequency, and (c) 3D bundles in an AC field of 50 kHz frequency. The gold-coated, conductive hemispheres appear dark and bare, and dielectric hemispheres appear light. The electric field is applied in the vertical direction in the images. The scale bars in (a–c) are 50 $\mu$m.
Figure 5. Number of particles as a function of the particle orientation angle, \( \theta \), where the angle is determined by the angle between the gold/polystyrene interface and the direction of the electric field. Two high peaks in the angle distribution are observed at orientation angles of 0° and 180°, in line with the direction of the electric field.

of \((3\cos^2 \theta - 1)/2\) over all the particles.\(^{52}\) The angle, \( \theta \), is between the orientation vector of a given particle and the director \( \hat{n} \) (see inset of Figure 5). \( S \) is equal to unity in perfectly aligned ferroelectric and antiferroelectric phases and equal to zero in the isotropic phase.\(^{52}\) The polarization parameter \( P \) is given by

\[
P = \left| \frac{1}{N} \sum_{j=1}^{N} (\vec{e}_j \cdot \hat{n}) \right|
\]  

(1)

\( P \) can be expressed as the average of \( \cos\theta \) over all of the particles.\(^{53}\) \( P \) is equal to unity in a perfectly aligned ferroelectric phase and zero in the antiferroelectric phase. \( S \) therefore measures orientational order, and \( P \) distinguishes between ferroelectric and antiferroelectric phases. In a ferroelectric phase, \( P \geq S \), while in an antiferroelectric phase \( P < S \).

We measured the orientation angle for 727 particles by processing the optical digital image in Figure 3b. The instantaneous director \( \hat{n} \) was designated in the direction of the applied electric field, and the angle \( \theta \) was defined as the angle between the gold/polystyrene interface and the director \( \hat{n} \). The angle \( \theta = 0^\circ \) was designated for the case when the gold/polystyrene interface was fully aligned with the direction of the electric field and the gold-coated hemisphere was situated on the left side of the particle. The angle \( \theta = 180^\circ \) was designated for the case when the gold/polystyrene interface was fully aligned with the direction of the electric field and the gold-coated hemisphere was situated on the right side of the particle. The distribution of the orientation angle around \( \theta = 0^\circ \) and \( \theta = 180^\circ \) was determined. The number of particles at a specific orientation angle for the image processed is plotted in Figure 5. The two peaks in the number of particles at \( 0^\circ \) and \( 180^\circ \) orientation indicate that the particles orient with highly specific direction.

The orientation order parameter \( S \) for this image was calculated to be \( S = 0.98 \). This is very close to unity, which indicates that the crystal is in either of the well-aligned ferroelectric or antiferroelectric phases. To further characterize this 2D metalldielectric crystal, the polarization parameter \( P \) was calculated to yield \( P = -0.003 \), which indicates that the metalldielectric 2D lattice structures are in a well-aligned antiferroelectric lattice.

### 4. Modeling of Janus Particle Orientation and Staggered Chain Formation in an Electrical Field

We calculated the electric field distribution and the energy of the system for different particle configurations in order to understand why individual Janus particles orient in the direction of the electric field in such a manner and to model the formation of staggered chains. The total electric energy \( W_e \) of the system can be obtained by integrating the local energy density, \( W_{es} \) (defined in the Appendix), over the subdomain volume (V)

\[
W_e = \int_V W_{es} \, dV
\]  

(2)

Particles responding to dielectrophoretic force are attracted (if they are more polarizable than the media) to the high field intensity area in an electric field gradient so that the minimum potential energy is reached when the particles are closest to the point of highest electric field strength.\(^{54,55}\)

We performed a 2D FEMLAB simulation of a complex particle—dielectric system inserted inside a parallel plate capacitor, since our system consists of two electrodes separated by a dielectric media. We kept the voltage constant and only changed the orientation angle and/or the positions of the Janus particles to form different types of four-particle chain configurations. We then calculated the total stored electric energy (effective units of J m\(^{-1}\), since this was a 2D simulation and we integrated over the area rather than volume). This procedure was repeated until we found the configuration with a maximum in stored electric energy. We refer to this as a “quasi-Monte Carlo” approach: it is broadly similar to the methodology of a Monte Carlo simulation;\(^{56}\) however, since our system is quite complex and the energy calculations in each step require a very computationally expensive solution of a system of partial differential equations, we only model a few selected configurations and compare their energy.

The dielectric permittivity of the subdomains was calculated by means of the complex permittivity (which accounts for the frequency of the field) as given by Morgan et al.\(^{25}\)

\[
\varepsilon = \varepsilon_0 \varepsilon_r - \frac{i(\sigma)}{\omega}
\]  

(3)

where \( i \) is the imaginary unit, \( \sigma \) is the electrical conductivity, and \( \omega \) is the AC electric field frequency (for which we specified a value of 10 kHz). The dielectric subdomains specified in FEMLAB and the details of the conductivity and permittivity values used are listed in the Appendix. The top and bottom electrodes were energized in the simulations with \( \pm 0.1 \) V in the case of the particle orientation simulation and \( \pm 0.25 \) V for the particle configuration simulation. In both cases, the effective field strength simulated within the cell was 100 V cm\(^{-1}\). The boundaries on the sides of the experimental cell were taken to be electrically symmetrical.

**Orientation Angle Simulation.** To understand why an individual particle is oriented with its gold/polystyrene interface aligned with the electric field, we calculated the electric energy of the system containing a single particle at different orientation angles (Figure 6). The 0° orientation angle (Figure 6 inset) was taken as the baseline, since this was the equilibrium orientation
angle that was observed experimentally. The total electric energy of the system was calculated from $-90^\circ$ to $90^\circ$ by rotating the particle about its gold/dielectric interface axis in $5^\circ$ increments. The potential energy is maximal at $-90^\circ$ when the gold/polystyrene interface is perpendicular to the electric field direction. The energy difference decreases as the particle is incrementally rotated to $0^\circ$, which results in the minimum in potential energy of the system. This corresponds well to the experimentally observed orientation of the particles (Figures 3a and 5), which is between $-10^\circ$ and $10^\circ$. We multiplied the total integrated electric energy of the system by the particle radius (2.5 µm) to estimate the total energy of the system (effective units of J, converted into units of thermal energy $kT$). The potential energy difference between $-90^\circ$ orientation and $0^\circ$ orientation angle was $\sim100kT$, which is a reasonable value for a body of this size that has been arrested from thermal or hydrodynamic fluctuations. This is equivalent to the induction of a dipole of maximal strength in the gold-coated hemisphere (aligned with the field) and is broadly similar to the alignment of elongated and rodlike particles along the electric field direction.23

**Particle Chain Configuration Simulation.** After establishing the origin of the orientation of an individual particle in the electric field, we simulated the energy profiles of different chain configurations of Janus particles to determine which one would result in the minimal potential energy of the system. In all configurations simulated, the gold/polystyrene interface of all Janus particles was aligned with the field direction, as we had established this orientation in the previous simulation. The baseline configuration included four Janus particles forming a staggered chain (Figure 7c), since this was the arrangement that was predominantly observed experimentally. For this baseline configuration, the gold shells touched slightly off-center (compared to a regular, straight chain) near the poles of the particle and the polystyrene half of each particle was facing in alternating directions. This base assembly is compared with the following alternative configurations in Figure 7: particles with gold shells directly in contact with the dielectric portion of adjacent particle within a straight chain (Figure 7a), gold shell directly in contact with the gold shell of an adjacent particle within a straight chain (Figure 7b), and gold shells touching more off-center in a staggered chain (Figure 7d).

The simulation shows that the minimum in potential energy difference does indeed occur for the experimentally observed configuration where the gold shells are in contact with each other slightly off-center in a staggered chain (Figure 7c). It appears that the gold-coated hemisphere (which is nearly infinitely polarizable) dominates in determining particle structures and dynamics at medium and high electric field intensities. After the particles orient to $0^\circ$ or $180^\circ$ to align their gold/polystyrene interface with the electric field, their gold-coated hemispheres are attracted to each other near the poles to align the largest dipoles (created within the gold coating) with each other along the electric field lines. The particles alternate with the polystyrene half of the particle on the left and right sides so that only the gold shells are in contact with each other, minimizing the potential energy of the chain configuration and resulting in a narrow conductive lane throughout the length of the chain. When the

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**Figure 6.** Effect of orientation angle of the particle on the calculated potential energy difference. The inset simulation illustrates the electric energy density contour around a single Janus particle at a $0^\circ$ orientation angle in one half-cycle of an AC electric field. The direction of the electric field is indicated on the simulation image, and the yellow arc on the left side of the particle represents the gold shell. The other half of the particle was simulated with a counterionic layer.

**Figure 7.** Simulations of the electric energy density contours around different particle configurations (a–d) of four Janus particles in one half-cycle of an AC electric field and the effect of particle configuration of four particles on the potential energy difference (e). The bar to the right indicates the intensity of the electric energy density in $\text{J m}^{-3}$, and the direction of the electric field is indicated on each simulation. The yellow arc represents the gold shell in (a–d).
particles are situated so that their point of contact is further off-center within a staggered chain where the gold shells are in contact (Figure 7d), the potential energy increases dramatically. The potential energy of the system for configuration B where the gold shells are on the same side of a nonstaggered chain (Figure 7b) is closest to the system that exhibits the minimum in potential energy. This type of chain is similar to the chains found in a type of Janus crystal with broader metallic lanes observed experimentally (Figure 4b), although in Figure 4b there are two sets of chains grouped together, which may be a kinetically trapped configuration.

Overall, the particle orientation and particle configuration simulations agreed well with the experimentally observed results. The same simulations were also performed in vacuum, without accounting for the counterionic conductance of the bare side of the Janus particle and the complex permittivities of the subdomains. We obtained a qualitatively similar result as for the simulations performed in water, for which we take into account the complex permittivity of each of the subdomains. Thus, the presence of the counterion atmosphere on the dielectric half of the particles appears to modulate the interactions, but the high polarizability of the metal half is the leading effect in the assembly process. This approach could in the future be used to predict the orientation and assembly of various anisotropic and patchy particles in applied electric fields.

5. Conclusions

The phase diagram for electric field intensity and field frequency for a monolayer concentration of Janus particles reveals five regions of particle behavior: disordered particles region, regular and staggered chains region, 2D crystallization region, induced charge electrophoresis (ICEP) region, and 3D bundles region. The staggered chain and 2D crystallization regions were further investigated by using electrostatic simulations to calculate the electric energy of the system to determine the most favorable particle orientation and lattice configuration. The simulations agreed with experimental observations and aided in the understanding of the Janus particle orientation along the direction of the electric field lines, and the staggered chain formation. The field-directed assembly of metallodielectric particles at high frequency could be used in the fabrication of photonic crystals of new symmetry types, massively parallel waveguides, liquid-crystalline films, and materials with directional electrical and heat transfer.

The rich variety of structures formed and dynamic motion of the metallodielectric Janus particles demonstrated here provide a glimpse of the interesting phenomena occurring when anisotropic particles are subjected to external fields. The metal-coated hemispheres of the particles play a key role in the formation of different structures and in the electrohydrodynamic mobility of the particles once the electric field intensity within the experimental cell becomes strong enough to overcome Brownian motion. The experimental technique and simulations may now be applied to other types of anisotropic particles, which may form different types of novel structures and potentially lead to the fabrication of new materials.

Acknowledgment. This research was supported by an NSF-NIRT grant (CTS-0506701), and it is part of the NSF Nanoscale Interdisciplinary Research Team for nanoscale directed self-assembly in electrical and optical fields in collaboration with the University of Delaware and California Institute of Technology. We also acknowledge support from an NSF-CAREER grant (CTS-0238636,) and a Camille Dreyfus Teacher-Scholar award.

Appendix

Electric Energy Definition and Dielectric Subdomain Values Specified in FEMLAB

The electric energy of the system is directly related to the electric field intensity in the cell. The local electric energy density \( w_{es} \) for particles in vacuum is given by

\[
 w_{es} = \frac{1}{2} D E = \frac{1}{2} \varepsilon_0 E^2
\]

where \( D \) is the electric flux density, \( \varepsilon_0 \) is the dielectric permittivity of vacuum \( (8.854 \times 10^{-12} \text{ C}^2 \text{N}^{-1} \text{ m}^{-2}) \), and \( E \) is the electric field intensity.\(^{57,58}\) For our system, which is not in vacuum, the electric flux density \( D \) is given by

\[
 D = \varepsilon_r \varepsilon_0 E
\]

where \( \varepsilon_r \) is the relative permittivity.

The dielectric subdomains defined in FEMLAB were the water media \((\varepsilon = 78\varepsilon_0 - i(10^{-4}/\omega))\), a thin \((100 \text{ nm thickness})\) conductive counterionic shell \((\varepsilon = 78\varepsilon_0 - i(0.2)/\omega))\) on the bare polystyrene half side of the particle, and the two portions of the particle.\(^{19,59}\) These two parts of the particle include the dielectric polystyrene core \((\varepsilon = 2.55)\) and a very thin \((30 \text{ nm thickness})\) conductive gold shell \((\varepsilon = 10^6\varepsilon_0 - i(4 \times 10^4)/\omega))\) on one half side.\(^{25,59}\) By using a very high value for the polarization of gold, we effectively introduce a domain with high conductivity (i.e., ideal metal). The simulations confirm that this leads to complete suppression of the electric field in the metal shell, as expected for an ideally conductive metal.

Complex permittivity was not used for the polystyrene core, since its electrical conductivity is negligible \((\sim 10^{-19} \text{ S m}^{-1})\) and the constant bulk value of 2.55 was used for its permittivity.\(^{60}\) The gold metal coating was specified with bulk gold values for conductivity and permittivity (with \(\varepsilon \rightarrow \infty\) for a perfect conductor). For the Milli-Q water media, we used a value of \(10^{-4} \text{ S m}^{-1}\) for the conductivity and 78 for the permittivity.\(^{59}\) Carbon dioxide dissolved in the water in contact with air yields \(1.0 \times 10^{-3} \text{ S m}^{-1}\) for a constant value of 0.2 S m\(^{-1}\) for the permittivity of water.\(^{59}\) The total surface conductance is defined as

\[
 K_S = K_{S,d} + K_{S,d}
\]

where \( K_{S,d} \) is the conduction of the diffuse part of the double layer and \( K_{S,s} \) is the conduction of the Stern layer.\(^{25}\) \( K_{S,s} \) is calculated as

\[
 K_{S,s} = \sum_j \sigma_{qs,j} \mu_j
\]

where \( \sigma_{qs,j} \) is the surface charge density in the Stern layer of the double layer and \( \mu_j \) is the ion mobility.\(^{25}\) For the polystyrene particles used, the surface charge density \((\sigma_{qs})\) on the particle was 0.061 C m\(^{-2}\) (data from the vendor), and we used H\(^+\) and OH\(^-\) ions with mobilities from Morgan and Green, with \( \sigma_{qs,H^+} = 2.5 \times 10^{-7} \text{ m}^2(\text{V sec})^{-1} \) and \( \sigma_{qs,OH^-} = 3.63 \times 10^{-7} \text{ m}^2(\text{V sec})^{-1} \).\(^{25}\) The ion mobility would be lower in the Stern layer,\(^{57,58}\) Griffiths, D. J. Introduction to Electrodynamics; Pearson Education: London, 1999.


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but we use the bulk ion mobility values as an approximation. Since the double layer will consist primarily of a monovalent ion, we calculated an average value for $K_{S,s}$ of $1.73 \times 10^{-8}$ S based on averaging the value for $H^+$ and $OH^-$ ions. We used a value of $10^{-9}$ S for $K_{S,d}$ as the conduction in the diffuse layer obtained from Morgan and Green. The total surface conductance $K_S$ was calculated to be $1.83 \times 10^{-8}$ S, which was divided by the counterionic atmosphere thickness (100 nm) to yield a value of 0.2 S m$^{-1}$ for the conductivity of this counterionic layer. This surface conductivity value was consistent with data in the literature for very low electrolyte concentrations.$^{25,61}$

**Supporting Information Available:** Movies (in AVI format) illustrating the phase diagram transition from staggered chains formed at high frequency AC field to low frequency ICEP motion of the Janus particles in directions perpendicular to the applied electric field. The staggered chains disassemble, and the particles begin ICEP motion once the frequency is reduced from 25 to 1 kHz and the electric field intensity is raised from 60 to 150 V cm$^{-1}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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