Reconfigurable Assemblies of Janus Rods in AC Electric Fields

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Materials and Methods

Materials: Deionized (DI) water (18.2 MΩ-cm resistivity) is used in all experiments (Millipore Filter System, Model Z00QSV001). Ammonium hydroxide (25% in water) and tetraethyl orthosilicate (TEOS) are purchased from Acros Organics. Pentanol, polyvinylpyrrolidone (PVP, 40,000 molecular weight), $Na_2S_2O_3$, $K_4Fe^{II}(CN)_6$, and $K_3Fe^{III}(CN)_6$ are purchased from Sigma Aldrich. Ethanol (200 proof) and isopropanol are purchased from Decon Laboratories and BDH, respectively. Sodium citrate dihydrate, potassium hydroxide, and sodium chloride are purchased from Fisher Scientific. Polydimethylsiloxane (PDMS, Sylgard 184) monomer and crosslinking agent are obtained from Dow Corning.

Silica Rod Synthesis: Silica rods are synthesized following a modified one-pot technique developed by Kuijk and co-workers[1] and modified by Chaudhary and co-workers,[2] which is briefly summarized here. Synthesis begins with the addition of 300 mL of pentanol and 30 g of PVP to a 500 mL round bottom flask. The flask contents are ultrasonicated (Branson Ultrasonics) for 3-4 h until PVP fully dissolves. After ultrasonication, 30 mL of ethanol is added to the flask followed by the addition of 8.4 mL of DI water and 2 mL of 0.18 M sodium citrate dihydrate solution (5.3 g in 100 mL water). The flask is then gently shaken by hand 15-20 times to promote mixing between liquids to form an emulsion.

Monodisperse emulsion droplets are obtained when the emulsion is passed through a filter (0.1 μm pore, Membrane Solutions) and collected in a clean flask at a flow rate of 50 mL/h using a syringe pump (Harvard Apparatus). A volume of 6.75 mL of ammonium hydroxide is subsequently added to the filtered emulsion. The flask is shaken by hand 15-20 times before adding 3 mL of TEOS. The flask is again shaken by hand 10 times, sealed with a stopper, and left undisturbed for 17 h at 20°C.

When the reaction is complete, the synthesized silica rod suspension is transferred to 50 mL centrifuge tubes (VWR) and centrifuged at 3000 rpm for 1 h. The supernatant is then removed and 30 mL of ethanol is added to the centrifuge tubes and the silica rods are re-dispersed by vortex mixing followed by sonication for 10 min. The silica rods are centrifuged at 2000 rpm for 20 min followed by supernatant removal. Ethanol addition, re-dispersal, and centrifugation under these conditions are repeated twice. After the ethanol wash, 30 mL of DI water is added to the centrifuge tubes followed by centrifugation at 1500 rpm for 15 min. This process is repeated until the supernatant exhibits a neutral pH value.

Immediately following this initial synthesis process, the silica rod dimensions are 1.45±0.06 μm in length and 0.29±0.02 μm in diameter. To further improve their size uniformity, these rods are suspended in 30 mL of ethanol and centrifuged at 1200 rpm for 10 min. The supernatant is removed and this step is repeated approximately 5 times.

To increase the rod dimensions, additional silica layers are grown on the rods using a seeded Stöber process.[2] Monodisperse silica rods are added to 50 mL of ethanol in a 500 mL flask. The suspension is stirred using a magnetic stir bar. Next, 6 mL of ammonium hydroxide, 5 mL of DI water, and 0.5 mL of TEOS are added to the flask in succession. After 6 h, 0.12 mL of DI water and 0.5 mL of TEOS are added every 3 h. We typically perform 19 additions to achieve targeted rod dimensions of 2.3±0.2 μm in length and 1.11±0.08 μm in diameter. Silica rod suspensions of 5.7 wt% and 1 wt% concentration is prepared and used for side- and tip-coated Janus rod fabrication, respectively.

Preparation of Side-Coated Janus Rods: Side-coated Janus rods are prepared using the same technique that yields Janus spheres.[3] 50 μL of rod suspension at 1 wt% is settled onto a glass slide pretreated with piranha solution and dried quickly to form a sub-monolayer of rods. Thereafter, the sub-monolayer of rods is coated with 2 nm of titanium (Ti) followed by 15 nm of gold (Au) using an e-beam evaporator.

The side-coated Janus rods are further purified by selective etching for 60 s. The final purification is performed using an Au etch solution composed of 4.93 g $Na_2S_2O_3$, 0.0867 g $K_4Fe^{II}(CN)_6$, 0.667 g $K_3Fe^{III}(CN)_6$, 11.2 g KOH, and 200 mL of DI water. The substrate containing a sub-monolayer of coated rods is removed from the etching solution and submerged in a beaker of DI water, where it is rinsed vigorously for 30 s. The rinsing step is repeated to ensure that no etching solution remains on the substrate. The side-coated Janus rods are then released from the substrate by ultrasonication in DI water.

Preparation of Janus Matchsticks: Janus matchsticks are produced by first creating a vertically aligned monolayer of homogeneous silica rods placed between a 22 sq. mm indium tin oxide (ITO) coverslip electrodes (SPI supplies) with an 8-12 ohm sheet resistance. The ITO coverslips are washed thoroughly with isopropanol before experiments and dried using nitrogen gas. Conductive copper tape (Electron Microscopy Sciences) is cut into two 3 cm long strips and each attached to the conductive side of an electrode to act as leads for the function generator terminals. One electrode is placed flat on the microscope stage with two strips of double-sided adhesive tape (3M) on top and separated by 10 mm. A wooden applicator is used to gently apply pressure to the adhesive tape and ensure good contact.

A 6 μL volume of silica rod solution (5.7 wt% concentration) is pipetted onto the electrode and a second electrode is carefully placed on top. Care is used in placement since any contact between the copper lead of one electrode and the surface of the opposite electrode will create a conductive path that reduces the effectiveness of the electric field for assembly. The double-sided adhesive tape with a nominal 61 μm thickness serves as a spacer between the electrode pair. Additional single-sided adhesive tape is used to secure the ITO electrode cell and prevent the second electrode from accidental removal during the experiment. The conductive copper tape serves as leads to interface the electrodes with alligator clips and a BNC connector to the function generator (Agilent 33522A).

The silica rods are initially aligned vertically under electric field conditions of 100 kHz, 4 V. We manually decrease the frequency to 4 kHz over a 5 min period and allow the silica rods 10 min to equilibrate and form a hexagonally close-packed (hcp) structure. The frequency is further decreased to 1 kHz over a 1 min period to freeze the desired structure and allow system to dry in air for approximately 12 h.

A PDMS stamp is used to remove any rods that lie on top of the monolayer after drying. PDMS stamps are prepared by mixing Sylgard 184 monomer and crosslinking agents at a weight ratio of 10:1. All PDMS stamps are treated by oxygen plasma in a Harrick PDC-32G to induce the necessary adhesion and wettability. Typical parameters are a plasma power setting of 6.8 W, a chamber pressure of approximately 150 mTorr, and treatment duration of 50 s. The purification step consists of placing a plasma-treated PDMS stamp on top of the monolayer and pressing with uniform pressure for 20 s to remove the deposited rods.

Following initial purification, the substrate with the refined silica rod monolayer is placed in a Temescal electron-beam evaporation system, where it is coated with 2 nm of Ti followed by 25 nm of Au. A second plasma-treated PDMS stamp is used to remove the Au-coated rods for matchstick fabrication by applying a uniform pressure for 20 s.

A final purification is performed using an Au etch solution composed of 4.93 g $Na_2S_2O_3$, 0.0867 g $K_4Fe^{II}(CN)_6$, 0.667 g $K_3Fe^{III}(CN)_6$, 11.2 g KOH, and 200 mL of DI water. The stamp with the Janus matchsticks is submerged in a beaker of the etching solution for 240 s. The stamp is then removed from this solution and submerged in a beaker of DI water, where it is rinsed vigorously for 30 s. The rinsing step is repeated to ensure that no etching solution remains on the stamp. The Janus matchsticks are released from the stamp by ultrasonication in DI water.

AC Electric Field Assembly: Coverslips (Fisher Scientific) with dimensions of 24 mm x 50 mm and a thickness ranging from 0.13 mm to 0.16 mm are used as substrates for electrode fabrication. Square capillaries (Vitrocom) with 200 μm outer diameters are taped to the coverslips to act as masks for creating the gaps between individual electrodes. The coverslips are placed in a Temescal e-beam evaporation system and coated with 10 nm of Ti followed by 100 nm of Au. This technique produces electrode pairs with a gap of approximately 200 μm.

The electrodes used in our experiments are fabricated as described above and are washed with isopropanol prior to use. Adhesive tape is used to secure the electrodes to the microscope stage. Leads that interface to the function generator terminals are made from 3 cm strips of conductive copper tape, which are attached to the Au thin film. A silicone O-ring spacer is placed in between the electrode pairs. 10 μL of solution with a rod concentration of <1 wt% is pipetted into the O-ring, which is subsequently sealed using a 18 sq. mm coverslip.

The rods are given 5 min to sediment to the substrate surface before being subjected to an applied AC electric field of varying strength and frequency. Our observations indicate that the bare silica rods and Janus matchsticks responded well to 10 V, while the side-coated Janus rods and Janus doublets responded well to 3 V and 4 V, respectively. The rods are all initially subjected to a 100 kHz frequency and given at least 10 min to equilibrate. Changes in frequency are made in 200 kHz increments followed by equilibration until a frequency of interest is reached.

Finite Element Modeling: We used the AC/DC module in COMSOL Multiphysics modeling package to calculate the electric field and electric energy distribution around the complex Janus rod chains, using,

$$\nabla.\boldsymbol{J} = Q_j \tag{1}$$

$$\boldsymbol{J} = \sigma\boldsymbol{E} + j\omega\boldsymbol{D} + \boldsymbol{J_e}$$

$$\boldsymbol{E} = -\nabla V$$

where, $\boldsymbol{J}$ is the current density, Q_j is the current source, σ is the electrical conductivity, $\boldsymbol{E}$ is the electric field intensity, j is the imaginary unit, ω is the AC electric field frequency, $\boldsymbol{D}$ is the electric displacement, $\boldsymbol{J_e}$ is the external current density, and V is the electric potential. Electric Currents interface in AC/DC module provides a settings window, where material properties such as dielectric permittivity and electrical conductivity can be defined. Some simplifying assumptions are made before determining the interactions. We assume that our Janus rods remain confined to a quasi-2D configuration on the substrate surface to remove the complexity of 3D calculations.

The geometry of individual Janus building blocks are modeled as 2D cross-sectional top-view with a 100 nm shell of counterion layer and Au shell of respective thickness depending upon the patch type present in the Janus building block. In this way, the system was divided into four different domains: silica core, Au shell, counterion shell, and a water medium. A grid mesh is generated to solve for the applied potential distribution. The complex Janus rod chain is placed in the orientation of interest, relative to the electric field direction. We defined the dielectric permittivity of silica core to be 3.8 and water as well as the counterion layer to have a dielectric permittivity of 78.[4] For Au coating, we assume the dielectric permittivity to be 10^9.[5] We also defined the electrical conductivity of silica to be 10^{-18} S m^{-1}, the Au coating to be $4\text{x}10^7$ S m^{-1}, water to be 10^{-4} S m^{-1}, and the counterion layer to be 0.2 S m^{-1}.[5]

The electric field around the Janus rods is determined using Equation (1). Calculations are carried out for an AC electric field between top and bottom electrodes of 15 V/mm for the case of side-coated Janus rods, 20 V/mm for the case of Janus doublets, and 50 V/mm for the case of Janus matchsticks. In addition, AC electric field frequency is applied using the Frequency Domain settings window in AC/DC module. Figure S1 and Figure S2 show the results of our COMSOL Multiphysics modeling of electric energy density distribution around four different chain morphologies of side-coated and tip-coated Janus rods, respectively.

Supplemental Figures:

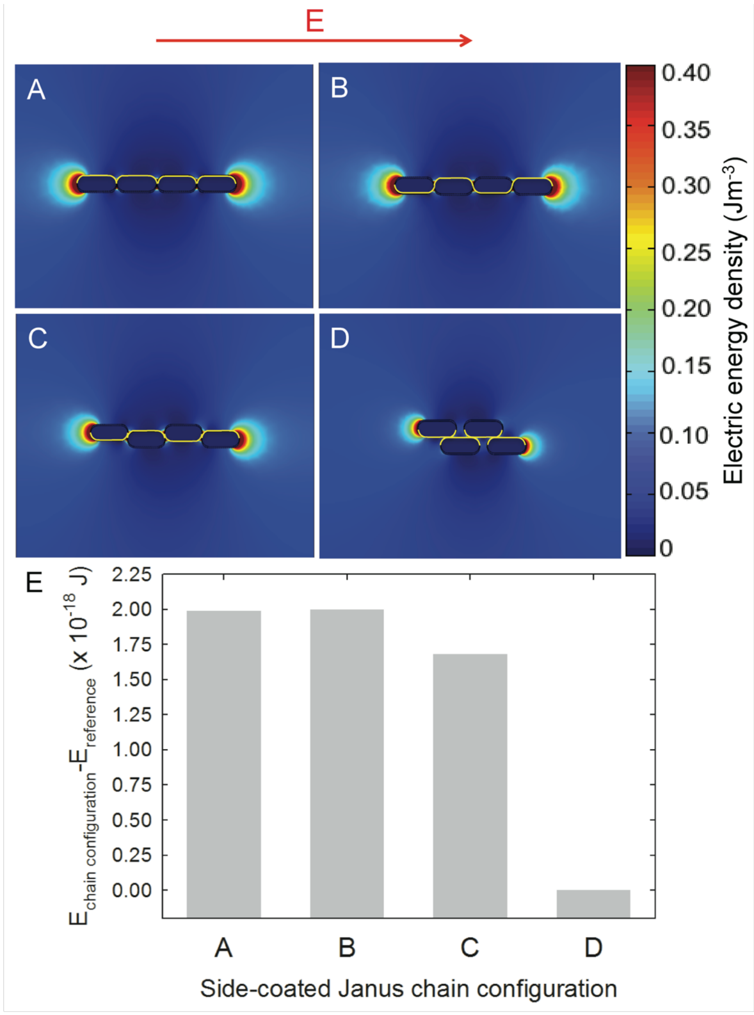

Figure S1. (A-D) Finite element modeling of electric energy density (Jm^{-3}) distribution around four different configurations of side-coated Janus rods at 15 V/mm, 100 kHz. (E) A plot of the potential energy of four chain configurations with respect to the experimentally observed (reference) configuration (D).

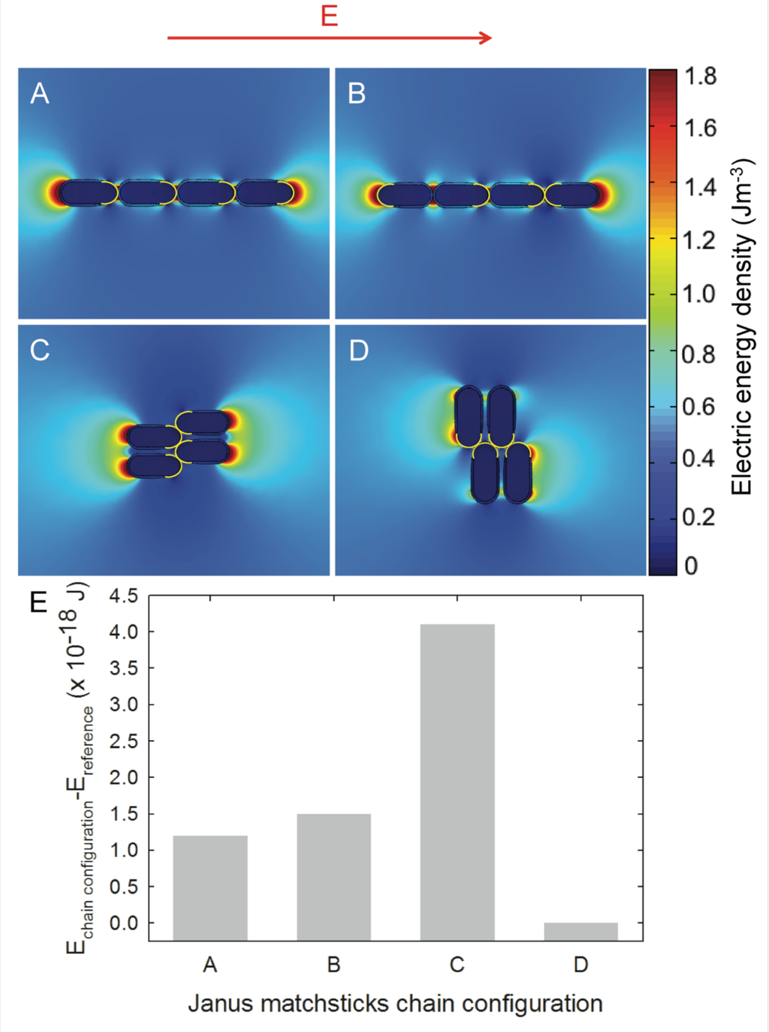

Figure S2. (A-D) Finite element modeling of electric energy density (Jm^{-3}) distribution around four different configurations of Janus matchsticks at 50 V/mm, 3.5 MHz. (E) A plot of the potential energy of these configurations with respect to the experimentally observed (reference) configuration (D).

Supplemental Movie Legends:

Supplemental Movie 1: Homogeneous silica rods assemble into linear chains that align with the electric field direction at 30 MHz, 50 V/mm. The movie speed is 4x.

Supplemental Movie 2: Side-coated Janus rods assemble into staggered chains with overlapping Au patches that align with the electric field direction at 100 kHz, 15 V/mm. The movie speed is 4x.

Supplemental Movie 3: Side-coated Janus rods assemble into reconfigurable staggered chains that align with the electric field direction at 100 kHz, 15 V/mm. The electric field is turned off for ~10 s and the particles in the staggered chain disperse by Brownian motion adopting random orientations in suspension. The electric field is turned on again and the particles are allowed reassemble into staggered chains for ~20 s before turning off the field again for another ~10 s. The movie speed is 4x.

Supplemental Movie 4: Janus doublets assemble into flexible linear chains that align with the electric field direction at 100 kHz, 20 V/mm. The movie speed is 2x.

Supplemental Movie 5: Janus matchsticks assemble into bilayer chains at 3.5 MHz, 50 V/mm. Each Janus matchstick within the bilayer chain is oriented perpendicular to the electric field direction. The movie speed is 4x.

Supplemental Movie 6: Janus matchsticks assemble into reconfigurable bilayer chains at 3.5 MHz, 50 V/mm. The electric field is turned off for ~10 s and the particles in the bilayer chain disperse by Brownian motion adopting random orientations in suspension. The electric field is turned on again and the particles are allowed to reassemble into bilayer chains for ~50 s before turning off the field again for another ~10 s. The movie speed is 4x.

References

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