Electronic Supplementary Material (ESI) for Soft Matter.

Catalytically driven assembly of trisegmented metallic nanorods and polystyrene tracer particles

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Electronic Supplementary Information

Experimental Details

Electrochemical growth of trisegmented microrods

Metallic microrods consisting of three segments were grown electrochemically in anodic aluminum oxide (AAO) membranes by techniques described in previous reports. [1,2] Whatman Anodisc membranes (25mm diameter, area 490 mm^2) with a nominal pore size of 200 nm (actual pore diameter 300 – 350 nm) were used. By controlling the electrical current or potential as well as the electrodeposition time, rods of different composition and approximately identical length were prepared. In a representative synthesis, the branched side of the membrane was coated by e-beam evaporation with 350 nm of Ag, which served as the back contact for microrod electrodeposition. A sacrificial silver segment was electrodeposited into the membrane pores for 20 min. from a commercial Ag plating solution (Technic, Inc., 1025 RTU @ 4.5 troy/gallon) at a constant current density of -5.00 mA/cm^2 using a Ag plate in contact with the Ag evaporated film as the working electrode and a coiled Pt wire as the counter electrode. This gave silver segments approximately 20 µm in length. Following the deposition of the sacrificial Ag segment, Au and Ru segments were electrodeposited in the appropriate order, using constant current or potential, respectively, for Au and Ru, resulting in the product Au-Ru-Au and Ru-Au-Ru rods.

The deposition of Au was done using a commercial plating solution (Technic, Inc., Orotemp 24 RTU Rack) at a constant current density of -3.50 mA/cm^2 for 13 min., using the two-electrode setup described above for Ag. In order to electrodeposit Ru, a three-electrode setup was utilized with the Ag plate serving as the working electrode, a coiled Pt wire as the counter electrode, and a Ag/AgCl reference electrode. The electrodeposition was done at a constant potential of -0.65 V vs. Ag/AgCl using a commercial plating solution (Technic, Inc., Ruthenium U Solution 6.5 grams/quart) for 30 min. The plating cell was rinsed several times between depositions with deionized water. The average length of the AuRuAu rods was 3.7 ± 0.5 µm, with Au segments 1.4 ± 0.5 µm, and Ru segments 1.1 ± 0.4 µm. For the RuAuRu rods the average length was 3.3 ± 0.5 µm, with Ru segments 1.0 ± 0.3 µm, and Au segments 1.4 ± 0.17 µm. The as-deposited membranes were first nitric acid-etched (8 M for 10 min) to remove the Ag backing and sacrificial segments, followed by dissolution of half of the AAO membrane using NaOH solution (3 M for one hour). Once released the rods were washed several times by centrifugation using millipure water (18.2 MΩ-cm) until neutral pH was achieved. After rinsing, the suspension was stored in 10 mL of water, at an approximate microrod number density of 10^8/mL

Powered assembly in nanorod pusher and puller suspensions

The rod suspensions in water were added to H_2O_2 solutions to obtain a final concentration of 10%. This suspension was transferred into a capillary tube (Vitrocom) with a rectangular opening with dimensions of 2 mm x 0.200 mm. The tube was then mounted atop a silicon wafer for observation. The motion capture analysis was done as described in earlier publications. [2-4] Videos were taken at 30 frames per second with an Olympus BX60M microscope in both bright and dark field. The sample mixture was sonicated briefly (~ 10 s) prior to drawing into a capillary tube to break up any aggregates that form upon standing. The rapid aggregation of particles driven by catalytic decomposition of H_2O_2 means that the videos must be recorded quickly and explains why not all of the energetically favorable structures could be captured on video (e.g., Figure 3A, configuration 5). Particle coordinates are recorded by Physmo (open source software, http://physmo.sf.net), and analyzed with Microsoft Excel.

Assembly of trisegmented nanorods with polystyrene tracer particles

Experiments using charged tracer particles were done to investigate the balance of catalytically induced flow and electrostatic interactions in controlling particle assembly. 1 μm diameter polystyrene spheres with a negative surface charge (ζ = -63 mV) (Sigma, 2% aqueous suspension) were mixed with catalytic microrods and observed in bright field. The concentrations of rods and H_2O_2 were maintained the same as in the rod-rod interaction experiments (10%), while also incorporating ~ 0.3% PS spheres into solution. The mixture was observed in bright field under the same tracking conditions as described above. The samples were sonicated briefly before the videos were recorded.

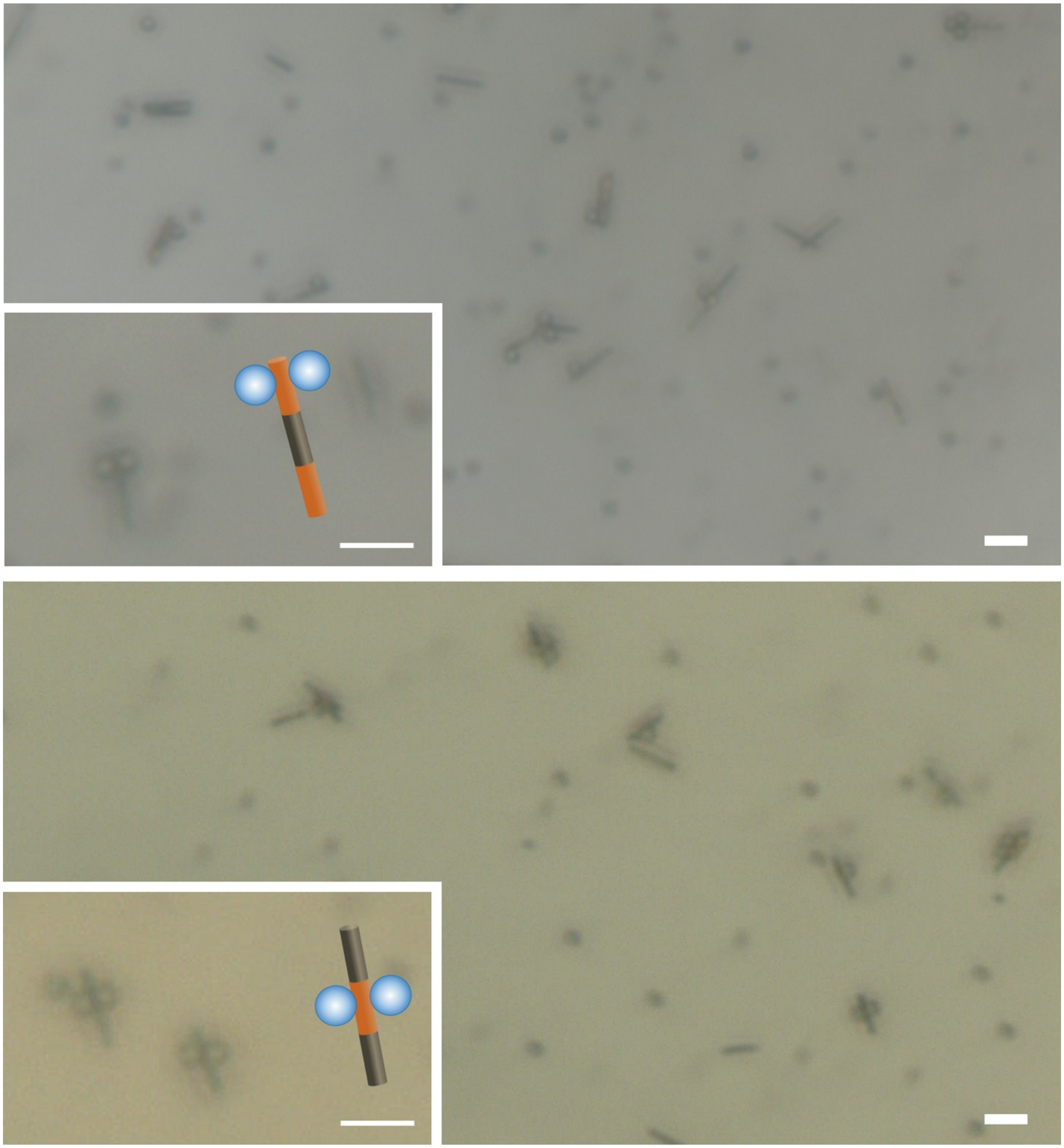
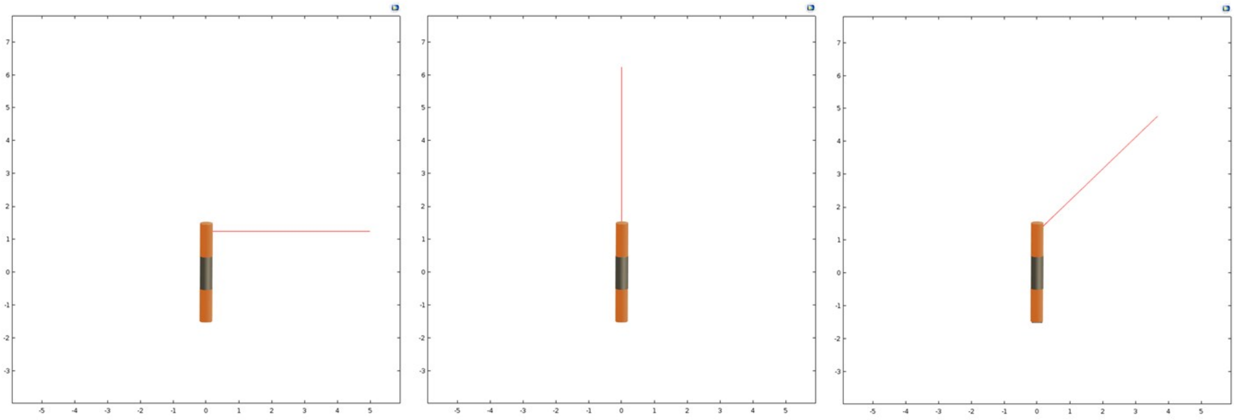


Figure S1. Optical microscope images of puller (top panel) and pusher (bottom panel) rods showing wide field snapshots of rod-sphere interactions (scale bar = 4 μm) along with insets at higher magnification that show more clearly the preferred orientation of the spheres on each type of rod (scale bar = 4 μm).



	Along Right			Along Top			Along 45 degrees		
Distance away from rod (µm)	0.5	2	5	0.5	2	5	0.5	2	5
Electrophoretic velocity (µm/s)	12.01	-0.13	0.12	11.93	0.95	0.11	20.37	1.29	0.1
Convective velocity (µm/s)	4.06	-0.43	-0.19	1.39	0.84	0.26	6.34	0.87	0.14
Total velocity (µm/s)	16.07	-0.56	-0.07	13.32	1.79	0.37	26.71	2.16	0.24

Figure S2. Axisymmetric COMSOL simulations (with superimposed cartoons of microrods) of three different paths that polystyrene tracer particles could take to approach puller rods. Tracer particle speeds at different distances along the line were calculated for both the electrophoretic and convective velocity components in the 2D Comsol model. Results are shown in Table S1.

Table S1. The data obtained from 2D COMSOL simulations, showing the contributing velocity components and total velocity of tracer particles at various distances from the tip of the rod. The electrophoretic velocity component is dominant at shorter distances. The positive velocity direction is defined as the tracer moving towards the rod.

Details of Numerical Simulations

Finite element simulations were done using the COMSOL commercial simulation package. The model was modified from the earlier work of Posner and coworkers (5, 6), and the details can be found in our previous paper (2). In the 2D model used in this work, protons are generated and consumed at the Au (anode) and Ru (cathode) ends of the nanorod, respectively. As a result of the distribution of the positively charged protons, an electric field is generated that points from the Au end to the Ru end. Since the nanorod carries a negative surface potential (zeta potential set to be -50 mV), the electric field leads to a surface electroosmotic flow along the long axis of the nanorod from Au to Ru. The distribution of ions and electrical charges, as well as the fluid flow, were simulated simultaneously by COMSOL, and in the end the fluid flow profile around the nanorod was generated by the simulation. The equation we used for the various modules in the COMSOL simulation software and different boundary conditions are listed below.

The proton distribution originates from a combination of proton generation at the anode and consumption at the cathode, and is further affected by the diffusion, convection and migration of protons (S1a). In our model this is solved with the continuity equation (S1b) at steady state:

$$J_i = uc_i - D_i \nabla c_i - \frac{z_i F D_i c_i \nabla \phi}{RT} \qquad (S1a)$$

$$\nabla \cdot J_i = 0 = u \cdot \nabla c_i - D_i \nabla^2 c_i - \frac{z_i F D_i \nabla \cdot (c_i \nabla \phi)}{RT} \qquad (S1b)$$

where ***u*** is the fluid velocity, F is the Faraday constant, ϕ is the electrostatic potential, R is the gas constant, T is the temperature and c_i, D_i, z_i are the concentration, diffusion coefficient, and charge of species i, respectively.

The electric field **E** (**E** = - $\nabla \phi$) in Eqn. S1 is calculated using the Poisson equation:

$$-\varepsilon_0 \varepsilon_r \nabla^2 \phi = \rho_e = F(z_+ c_+ + z_- c_-) \qquad (S2)$$

where z_+=1 and z_-=-1, ρ_e is the volumetric charge density, F is the Faraday constant and c_+ and c_- are the concentrations of the proton and the counter ion (HCO_3^-), respectively.

The fluid velocity outside the electrical double laeyr (EDL) is governed by the incompressible Navier-Stokes equation at steady state:

$$\rho(u \cdot \nabla u) = -\nabla p + \mu \nabla^2 u \qquad (S3)$$

where ρ is the fluid density, u is the fluid flow velocity, p is the pressure, and μ is the dynamic viscosity.

At the nanorod "surface" – which is actually at the edge of the EDL, but for thin EDLs is geometrically at the same location as the surface – the boundary condition is set so that the electric potential is 0, and the electroosmotic boundary applies. The four outside boundaries of the box are set to have the bulk ion concentration, and zero electrical potential. The top and bottom two sides are set to be open boundary so fluid can freely move in and out, and the left and right sides are set to be slip boundary. The proton flux normal to the surface is set to be positive on the anode and negative on the cathode to represent proton production and consumption at the two ends, respectively. The flux on the two metal surfaces are opposite in signs, and the overall flux is 0. For example, in the Au-Ru-Au system the proton flux on Au surface was set to be 0.5×7.0×10^{-6} mol/(m^2 s) while the flux on Ru surface was set to be 7.0×10^{-6} mol/(m^2 s), in order to achieve mass and charge conservation.

Major assumptions of the current COMSOL model are:

1. The first dissociation of carbonic acid is considered to be the equilibrium that balances the concentration of protons and the counter ion HCO_3^-, governed by equation (S4):

   $$CO_{2(aq)} + H_2O_{(l)} = H^+_{(aq)} + HCO^-_{3(aq)},\ K_a = 4.5 \times 10^{-7} \qquad (S4)$$

   Since the experiment was conducted without purging out CO_2, the starting pH of the solution is close to 5.65, the equilibrium pH of water saturated with ambient atmospheric CO_2. Therefore the bulk concentrations of proton and bicarbonate ions can be calculated to be 2.24×10^{-6} mol/L each. This gives a more accurate simulation result than assuming a starting pH of 7 and an equilibrium between only H^+ and OH^-. The flux of HCO_3^- on the nanorod is set to zero.

2. As was adopted in ref. 1 and 2, we assume the flux at the electrode surface is uniform in the sense that the incoming and outgoing proton flux at the cathode and anode do not vary over time or location. It was found that such a simplification does not stray far from reality (5), and for modeling catalytic pushers and pullers it is considered sufficiently accurate.

3. The thin double layer approximation was used to calculate the nanorod motion in H_2O_2. Therefore the intrinsic distribution of protons around the rod as a result of surface charge is not considered towards the final proton profile. Instead the final proton concentration profile is only created by proton generation at the anode and consumption at the cathode. In addition the zeta potential on the rod surface does not contribute to the electric potential calculations, since at the edge of the EDL, the potential has been screened to zero.

We used the commercial software COMSOL (version 5.0) to solve the H^+ and HCO_3^- concentration distributions, the electric field and fluid speed. The Electrostatics Module, Transport of Diluted Species Module, and Creeping Flow Module were the physics used in building the overall model. In our simulations, the trimetallic rods are 3 μm long with each segment of 1 μm, and the diameter of the rods is set to be 300 nm. We used axi-symmetric 2D models for the simulation of individual trimetallic rods, which are placed in a square box of 50 μm length on each side. Regular 2D models were used for the simulation of two rods in various configurations, and in this case the box was 25 μm on each side. 3D models were not used for the simulation of two rods because we were not able to achieve satisfactory convergence.

A 2D axi-symmetric model of a Au-Ru-Au rod was used to simulate the migration of a charged tracer particle towards the active trimetallic rod, as well as to estimate the relative contribution of electrophoretic migration vs. convective transport. A cutline of 5 μm length was drawn in the simulation result at three different angles as shown in Fig. S2. The electrophoretic velocity (***U***) of the tracer particle in Fig. S2 was obtained from the Smoluchowski equation

$$U = \frac{\zeta \varepsilon_r \varepsilon_0 E}{\mu} \qquad (S5)$$

where ζ is the zeta potential of the tracer particle (measured to be -63 mV), $\varepsilon_r \varepsilon_0$ combined is the electrical permittivity of the medium, ***E*** is the electric field, and μ is the dynamic viscosity of the medium. By extracting the electric field strength along the cut line from COMSOL and substituting that value into S1, we can obtain the electrophoretic speed of the tracer particle at each point along the cut line. On the other hand, the convective speed, which is simply how fast the fluid flows at any given point along the cutline, can also be extracted directly from the COMSOL result.

Supporting Videos

Video S1. Assembly of three PS spheres onto a single AuRuAu puller taken in bright field mode. The width and height of the frame are 36.5 and 32.7 µm, respectively. This video corresponds to the tracking data and plot analysis displayed in Figure 4. The assembly of all three spheres occurs within a time span of ~ 5 s. The accumulation of PS spheres on puller-type rods occurred at both ends of the microrods, which could accommodate several spheres at each end.

Video S2. Behavior of PS interacting with a single RuAuRu pusher, recorded in bright field mode. The width and height of the frame are both 25.6 µm. In this video, the tracer comes perpendicularly inward to the rod and makes an orbit before attaching to the Au segment. This was the most commonly observed mode of approach from the tracer particles, as predicted in the 2D COMSOL simulations of fluid flow.

Video S3. Various assembly interactions of AuRuAu pullers captured in bright field mode. The width and height of the frame are 58.2 and 32.7 µm, respectively. Throughout the video the interaction of pullers can be observed, as well as the theoretically predicted angular alignment into larger clusters. At the end of the video (~ 36 s) the assembly of three separate sets of dimers in which the Au segments overlap can be observed. This is the structure that is most frequently observed, and is consistent with the 2D COMSOL simulations shown in Figure 3.

Video S4. Short video showing the assembly of three RuAuRu pushers into a single trimer raft taken in bright field mode. The width and height of the frame are 43.5 and 32.7 µm, respectively. Hydrodynamic forces alone would bring pusher rods together with all segments overlapping, but electrostatic repulsion leads to a staggered configuration.

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