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Janus Colloidal Matchsticks

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Supporting Information

ABSTRACT: We fabricated chemically and shape-anisotropic colloids composed of silica rods coated with gold tips using a multistep process involving electric-field alignment and crystallization, microcontact printing, and selective metallization. Through direct observation, we found that these "Janus matchsticks" self-assemble into multipods (bi-, tri-, and tetrapods) of varying coordination number and patch angle in aqueous solution.

Information-encoded colloids are an emerging class of materials that enable the directed self-assembly of novel structures not accessible from their homogeneous counterparts. Recently, this concept has been demonstrated using Janus and triblock spheres whose patch size, location, and chemistry are precisely controlled.[1−3] For example, Janus spheres self-assemble into colloidal clusters of varying coordination number or wormlike chains depending on the solution conditions (e.g., pH, salt concentration).[4] Simply changing the patch motif to form triblock spheres causes entirely new structures to arise.[5] However, this prior work has been limited solely to spherical building blocks.

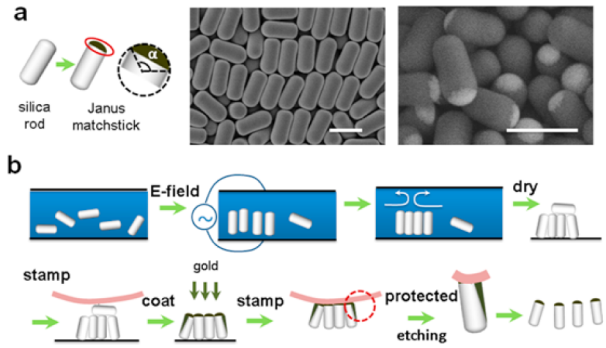
If anisotropic patchy colloids could be prepared with shape, size, and patch uniformity, new directions for self-assembly would be enabled. The simplest example of interest is colloidal rods. Indeed, Janus rods have already found use in cargo delivery,[6] single-molecule electrical sensing,[7] catalytically driven transport,[8] and nanoscale barcodes;[9] however, in these applications, polydispersity does not interfere with function. Here, building on a method for synthesizing silica rods,[10] we demonstrate a versatile fabrication route to produce monodisperse "Janus matchsticks" consisting of silica rods coated with gold tips. Upon suspending them in water, we observed the formation of multipod clusters of varying coordination number and phase angle that have no simple equivalent for spheres.

Our fabrication approach consists of three steps (see Scheme 1). First, we synthesized colloidal silica rods using a modified one-pot method recently reported by Kuijk and co-workers.[10] In the initial growth step, silica rods with lengths (L) of 1.45 ± 0.06 μm and diameters (D) of 0.29 ± 0.02 μm were created. These rods were used as seeds in subsequent growth steps[11] to produce approximately 1 g of silica rods (36% yield) with final dimensions of L = 2.3 ± 0.20 μm and D = 1.11 ± 0.08 μm. The method is general and can be used to produce rods with larger aspect ratios.

In the second step, we aligned the silica rods with their long axes perpendicular to a solid substrate in a uniform arrangement that persisted in the vacuum environment needed for their end-functionalization. Because silica rods naturally sediment in water to adopt a planar configuration (see the scanning electron microscopy (SEM) image in Scheme 1a), we applied an alternating current (AC) electric field ($\mathbf{E}$) to induce their vertical alignment and then condensed them into hexagonally close-packed (hcp) domains by electro-osmosis. Decreasing the frequency increased the electro-osmotic flow velocity, pushing domains toward the substrate and keeping them in a stable, aligned state during drying (Scheme 1b, top). A final step to remove misaligned rods yielded a nearly monodisperse set of building blocks for self-assembly (Scheme 1b, bottom). This step was accomplished by applying a polydimethylsiloxane (PDMS) stamp to the top of the dried layers; misaligned rods adhered to it and were removed when the stamp was detached. The stamp was rendered especially sticky by an oxygen plasma pretreatment (see Materials and Methods in the Supporting Information (SI)).

In the third fabrication step, we end-functionalized the exposed tips of the rods by electron-beam coating, first applying a thin titanium adhesion layer (2 nm) and then a gold layer (25

Scheme 1. Fabrication of Janus Colloidal Matchsticks[a]



[a](a) Schematic (left) and SEM images of non-functionalized (middle) and gold-tip-coated (right) silica rods (L/D = 2.1). The patch angle (α) was approximated assuming a spherical cap. Scale bars are 2 μm. (b) Schematic view of fabrication pathway for transforming silica rods to Janus matchsticks. First, the rods were aligned in an AC electric field and dried (top). Next, misaligned rods were selectively removed using a PDMS stamp (bottom, left). The remaining rods were successively coated with a titanium adhesion layer (2 nm) and a gold layer (25 nm) (bottom, middle). Finally, the rods were picked up using a PDMS stamp, which was used to protect their tips during selective gold etching.

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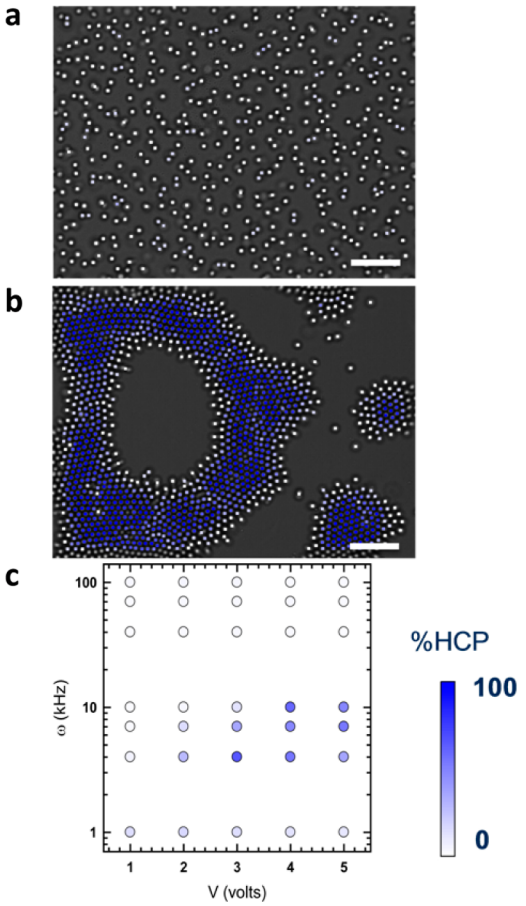

Figure 1. Electric field alignment of colloidal rods. (a) To align the rods, an AC electric field (100 kHz, 4 V) was applied across a 61 μm thick cell. The image shows a top-down view. (b) To generate positional order, the frequency was lowered to 10 kHz, producing hcp domains. The image shows hcp domains (blue) with disordered boundaries (white). (c) The fraction of hcp order, color-coded as shown, depended on the final frequency and voltage. The scale bars in (a) and (b) are 10 μm.

nm) in the same manner used previously to create Janus spheres.[12] There are subtleties to this procedure, as gold may also deposit on the long side of rods that are slightly tilted (see Figure S2 in the SI), introducing unacceptable patch polydispersity. To mitigate this, we protected their functionalized ends by applying a second PDMS stamp and then subjecting the rods to a gold etch, as was done previously for Janus spheres[13] (see Scheme 1b). After completion of the gold coat/etch steps, the Janus matchsticks were released from the stamp by sonication. We found the matchsticks to be monodisperse with a patch angle (α) distribution of 116° ± 12°. The overall yield for conversion of silica rods to Janus matchsticks was roughly 65%. When these purification steps were not performed, the mixture of Janus matchsticks and side-coated rods failed to form the structures reported below (see Figure S2).

The step involving electric field alignment was optimized as follows. When the colloidal rods are suspended between indium tin oxide (ITO) electrodes in deionized water in the presence of a field $\mathbf{E}$, they experience a torque $\mathbf{T} = \mathbf{p} \times \mathbf{E}$, where the dipole moment scales as $\mathbf{p} \sim L^3\mathbf{E}/\ln(4L/D)$, in which L/D is the rod aspect ratio.[14] The strong dependence on L sufficed to align the silica rods at frequencies above 10 kHz (Figure 1a).

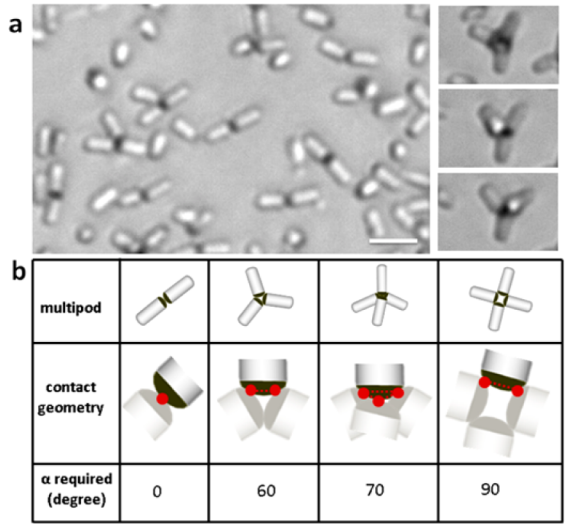

Figure 2. Janus matchstick self-assembly in aqueous solution (4.4 mM NaCl). (a) Optical images of bipods and tripods coexisting with tetrapods. The right panel shows a time-resolved series of optical images of a tetrahedral cluster as it rotates by Brownian motion. (b) Schematic table showing the *minimum* patch angle required for each multipod configuration.

We then took advantage of the fact that at 10 kHz and below, an electro-osmotic flow generated by counterion motion within the electric double layer[15] encourages the aligned rods to pack into hcp domains (Figure 1b). The number of rods coordinated by six nearest neighbors (denoted in blue in Figure 1b) was quantified through image analysis[16] under various conditions, as summarized in Figure 1c. We found the optimal conditions to lie in a frequency range of 10−100 kHz at 4 V, that is, we first promoted their vertical alignment at 100 kHz, then lowered the frequency to 10 kHz to induce hcp packing, and finally dried them at 1 kHz. This sequence was necessary because merely subjecting the rods to a 1 kHz frequency at 4 V produced neither the desired rod alignment nor hcp packing.

Our observations of the self-assembly of these monodisperse end-functionalized rods confirmed the generality of a valency rule tested previously using Janus spheres,[4] whose patch−patch attraction is akin to that of these anisotropic colloids. This rule dictates that structures at thermodynamic equilibrium with small coordination number will assemble into geometrical shapes dictated by the number of allowed nearest neighbors for each patch. Figure 2b shows the *minimum* patch angle required for the designated number of nearest neighbors for each possible multipod configuration. The experimentally observed structures, self-assembled at 4.4 mM NaCl, arise from a trade-off between sedimentation (which promotes a planar geometry), entropy (which promotes the greatest freedom to reorient within each matchstick cluster), and the attraction between the matchstick tips. At this ionic strength, the electrostatic repulsion between the rods (Debye length of 4.6 nm) was largely screened, thus bringing the rods into close enough proximity to activate their patch−patch attraction. The measured patch angle distribution (α = 116° ± 12°) exceeded the minimum patch angle required to form each of the multipods shown in Figure 2b, with planar assemblies of bipod and tripod geometries (Figure 2a, left) dominating their distribution. Despite the sedimentation of Janus matchsticks and their preference to adopt a flat conformation, we found that tetrapods assemble into a tetrahedral structure (Figure 2a,

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right) rather than a planar arrangement. We speculate that this shape arises from rotational entropy. The minimum two-dimensional rotation angle, $\Delta\alpha = 116° - \alpha$, is the difference between the measured patch angle of the gold-coated tips and the minimum patch angle required for a given multipod configuration. This convention reveals that the tetrahedron ($\Delta\alpha = 46°$) has higher rotational entropy than the planar arrangement ($\Delta\alpha = 26°$). These multipod structures, which were observed only when monodisperse matchstick colloids underwent self-assembly, validate the utility of our fabrication scheme, which minimizes side-coated rods to yield uniform Janus matchsticks.

In summary, we have presented a facile pathway for creating chemically anisotropic patches in a controlled location on colloidal rods that in principle can be generalized to particles of arbitrary aspect ratio, size, and shape. Since their geometrical shape and surface chemistry are anisotropic yet uniform from one building block to the next, complex structures self-assemble that are not accessible from either Janus spheres or chemically isotropic rods alone.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Methods and Materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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