Fabrication and Directed-assembly of Magnetic Janus Rods

Supporting Information

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EXPERIMENTAL

Materials and Characterization. Tetraethyl orthosilicate (TEOS) and ammonia (28 wt%) were purchased from Alfa Aesar. PVP (Mn=40000) was purchased from Tokyo Chemical Industry Co., Ltd. *n*-Pentanol was purchased from Acros. Hexadecyltrimethoxysilane (HDTMOS) was purchased from Adamas Reagent Co., Ltd. The water used throughout all the experiments was purified using the Millipore system. Other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. All of the reagents were of analytical grade and used without further purification. The morphology and structure of the samples were investigated using field emission scanning electron microscopy (SEM, S-4800) and transmission electron microscopy (TEM, JEM-2100) and confocal laser scanning microscopy (CLSM, FV1000-IX81). A neodymium iron boron (NaFeB) magnet (5 \times 50 mm, 25 \times 50 mm) was used to provide the magnetic field.

SEM sampling of the directed-assembly structures. The surface modified chess pieces were added into the mixture of ethanol (20 mL), water (3 mL) and ammonia hydroxide solution (1.1 mL, 28 wt%) under sonication. TEOS (70 μ L) was quickly injected into the mixture under mechanical stirring at 600 rpm. After 40 s, 2 mL of the mixture was transferred to a glass vial (15 \times 40 mm) and placed above a NaFeB disc magnet (25 \times 50 mm) with a distance of 2 cm for 20 s. The external magnetic field applied was 500 mT. After removal of the magnetic field, the sample was allowed to stay undisturbed for 15 min, after which it was washed with ethanol three times and dispersed in ethanol. In this case, the directed-assembly structures were fixed and ready to be characterized by SEM.

RESULTS AND DISCUSSION

Furthermore, steric effect can also be introduced into the assembly of these Janus rods. In the case of chess pieces-shaped paramagnetic Janus rods as building blocks, as shown in Figure S1,

Janus rods formed linear chains in magnetic field, as expected. Due to the steric repulsion between thicker rods, the rods could not lie alongside in the same plane. One rod must rotate by a certain degree to the neighbor one, to reach the optimum configuration. In this way, there are two possibilities for the third one next to the aligned two rods. As shown in Figure S1A, despite the two rods numbered 1 and 5, the rod 4 lied in another side of the rod 3, comparing with the rod 2. We name this configuration as "ABC". In contrast, "ABA" means that the rod 4 lies in repeating to the rod 2 (Figure S1B). We randomly selected 100 assembled morphologies as the statistical sample. According to the statistics, 51.2% of the morphologies were "ABA" and the others were "ABC". These preliminary results suggest that the odds of two morphologies was similar. This is reasonable since both hydrophobic-hydrophobic attraction and steric repulsion are short-range interactions. They can only dominate the relative configuration of the two neighbor rods. Regretfully, due to the small size of building blocks, we coated the colloidal assembly with silica by a subsequent hydrolization of TEOS in assembly system to fix the assembly structures, for SEM imaging. During the hydrolization of TEOS, the limited Brownian movement resulted in deviation from the optimum, especially for those rods at the end of aligned chains. Also long chains were difficult to be obtained.



Figure S 1. SEM images two assembly units as A) "ABC" and B) "ABA".



Figure S 2. Hysteresis loop of Fe₃O₄ microspheres.

In the water/PVP/*n*-pentanol (WPN) system, water can be bound by PVP in aqueous solutions with a high concentration of PVP, wherein water does not act as a solvent in the usual sense. Indeed, it is customary to refer to such water as "bound" water. Therefore, we can confine the hydrolysis of the silica precursor along with PVP by binding water with PVP in the WPN system. Similar to

the Janus rods synthesis, firstly, hydrolysis of TEOS took place in this thin layer of PVP-bound water, and resulted in a uniform silica shell on the surface of the seed particle. However, increasing the water content to a certain level (2 mL), no deweting occurred in subsequent hydrolysis and the obtained particles showed spherical morphology. It is believed that this change was attributable to an altered interfacial tension.



Figure S 3. SEM image of Janus rods obtained with increased amount of the added pure water to 2 mL.

Table S1 The length changes of Janus rods with hydrolysis time.

