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Non-spherical Janus microgels driven by thiolated DNA interactions

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ABSTRACT

Janus poly (*N*-isopropylacrylamide)-*co*-acrylic acid/Au microgels that resemble a "snowman", "dumbbell", and an "abalone" were prepared by thermally evaporating a layer of Au on half of the microgel surface, followed by exposure to thiolated single-stranded DNA with complementary sequences. We hypothesize that when the complementary single-stranded DNA attached to the Au forms the more stable double strand, the Au reorganizes on the microgel surface, yielding the observed unique Janus particle structures.

1. Introduction

Named after the two-faced Roman God Janus, the simplest Janus particles [1,2] have one half of their structure chemically and/or physically modified independent of their other half. Additionally, more complex "Janus-like" structures have also been generated [3–17] The anisotropy of Janus particles makes them suitable for unique applications [3–8] such as spatially-controllable chemical reactions [6b,c] asymmetric catalytic systems [3c,4b,c], self-assembled hierarchical structures [3a,b,6a,7a], and biomimetic colloidal building blocks [5a,b,7b,8b]. During the past decade, numerous techniques have been established to synthesize Janus particles [9–17], including microfluidic assembly [9b,c,10a], emulsion polymerization [11,12], masking coating [10b,c], and block copolymer self-assembly [14–17]. For example, Xu et al. [9c] generated monodisperse Janus particles (such as rods, disks, ellipsoids) via a microfluidic technique. Weitz et al. [11b] prepared triple rod, triangle, cone, diamond, and snowman-like particles in a well-controlled manner from emulsion polymerization. Granick [10b] achieved "matchstick" particles via asymmetric deposition. Although a plethora of Janus particles with controllable size/shape have been successfully achieved, it is still challenging to fabricate Janus particles with advanced functionality, using a facile protocol.

DNA has found its way into numerous applications due to its ability to be "engineered" via tailoring of the base sequences [8a,b]. DNA has been used as a template to position nanoscale components on the DNA double-strand backbone in well defined 1-D [18a], 2-D [18b], and 3-D patterns [18c] or as a linker to attach nanoparticles, proteins, and quantum dots to direct the formation of large periodic structures [19]. However, DNA isn't as prominent in applications involving the design and assembly of asymmetric nanostructures [8c–f]. Herein, we present a simple method to prepare functional hybrid Janus poly (*N*-isopropylacrylamide)-*co*-acrylic acid (pNIPAm-*co*-AAc)/Au microgels. To accomplish this, a thin layer of Au was thermally evaporated on microgels attached to a solid surface as shown in Scheme 1, which yielded microgels half coated with Au. The microgels were then removed from the surface and exposed to a mixture of two thiolated ssDNA molecules, which had complementary sequences. The thiol group is well known to attach to the Au layer, anchoring the DNA to the Au, and the presence of the complementary ssDNA chains induces the aggregation of the DNA. We found that these interactions were strong enough to re-arrange Au on the microgels to yield complex Janus microgels. Specifically, this treatment yielded particles that exhibited snowman-like, dumbbell-like and abalone-like morphologies.

2. Experimental

2.1. Synthesis of poly (N-isopropylacrylamide)-co-acrylic acid (pNIPAm-co-AAc) microgels

Microgels were synthesized following a previously published procedure. [20a] *N*-isopropylacrylamide (NIPAm) (11.9 mmol) and

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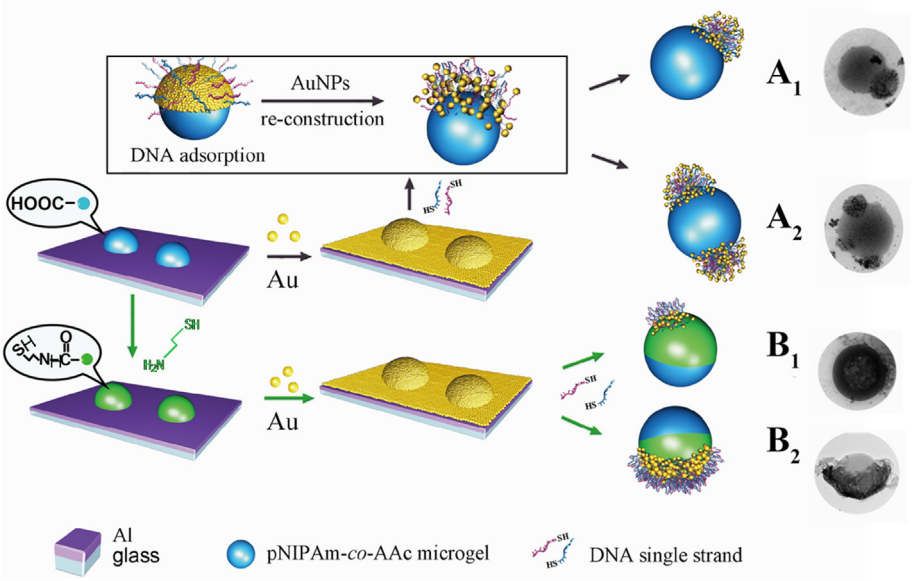

Scheme 1. Schematic of the formation process of the hybrid Janus pNIPAm-*co*-AAc microgels. The microgels were either (A1, A2) directly coated with Au or (B1, B2) were coated with Au after modifying the microgels with a thiol group. The process includes directional coating of an Au layer on a single side of microgel and subsequent DNA modification. (Far right), SEM images of the corresponding Janus particles.

N, *N*-methylenebisacrylamide (BIS) (0.703 mmol) and deionized water (99 mL) were charged into a three-necked round bottom flask. After 1 h of heating to 70 °C while bubbling N_2 gas through the solution, acrylic acid (AAc) (1.43 mmol) was added into the solution and immediately initiated by adding 0.2 mmol ammonium persulfate (APS), in 1 mL deionized water to the solution. The reaction proceeded for 4 h, and the resultant microgels were purified via centrifugation and resuspension in water 6×.

2.2. Coating of the Al-coated substrate with microgels

A single layer of pNIPAm-co-AAc microgels was deposited on the Al-coated substrate by "painting" a *dilute* solution of microgels onto the substrate. This was a slight modification to what was previously published [20b]. Following painting, the film was soaked overnight in deionized water to remove any microgels not directly adhered to the Al substrate. Subsequently, the film was washed copiously with deionized water to remove any excess microgels from the surface.

2.3. Functionalization of microgels with thiol

Functionalization was accomplished following previously published protocol [20c]. A layer of pNIPAm-co-AAc microgels attached to an Al-coated glass substrate was placed in pH 4.7 MES buffer (Pierce) and 9 mg cysteamine (Sigma–Aldrich, Oakville, Ontario) was added to the buffer. The solution and sample were allowed to mix while gently shaking for 1 h. Subsequently, 20 mg of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) was added to the system, and the reaction was allowed to proceed at 4 °C for 5 h. All samples were then rinsed with deionized water and soaked in pH 7.2 10 mM phosphate buffer saline solution (with 150 mM ionic strength from NaCl) for several hours to remove any unreacted reagents. The samples were again rinsed with H_2O and dried.

2.4. Coating microgels with Au

Au was added to the microgel via thermal evaporation (Torr International Inc., Model THEUPG, New Windsor, NY) at a rate of 0.1 Å s^{-1}. The thickness of the Au layer was varied from 0.6, 1.2, 1.5, 2.0–5 nm by controlling the evaporation time, and monitored via a quartz crystal microbalance.

2.5. Modification of microgels with DNA

All DNA was purchased from Integrated DNA Technologies. Prior to use, the disulfide functionality on the oligonucleotides was cleaved by dissolving lyophilized DNA in a DL-Dithiothreitol (DTT, obtained from Sigma–Aldrich) solution (0.1 M DTT, 0.18 M phosphate buffer (PB), pH = 8.0) at a mole ratio of 1:2 for DNA:DTT, and incubating at room temperature for 1 h [18d]. The cleaved DNA was purified using a PD-25 column, obtained from GE Healthcare Life Sciences. Subsequently, the purified thiolated DNA was added to the Au-coated microgels. We added ~10 nmol DNA_a in 250 μL buffer solution (0.01 M PBS, 0.01% SDS), and 10 nmol DNA_b in 250 μL buffer solution (0.01 M PBS, 0.01% SDS) to a solution containing Au-coated microgels (250 μL buffer solution, 0.01 M PBS, 0.01% SDS) according to the timing in the manuscript, and 20 min was allowed to pass before increasing the concentration of NaCl to 0.05 M using 2 M NaCl in 0.01 M PBS and SDS 0.01% while maintaining an SDS concentration of 0.01%. This process was repeated once more and then increased at 0.1 M NaCl increments until a concentration of 0.7 M NaCl was reached. The salting process was followed by incubation for 12 h at room temperature. To remove excess DNA, the Au-coated microgels were centrifuged and the supernatant solution removed, leaving a pellet of microgels at the bottom of the centrifuge tube. The microgels were then resuspended in fresh PB solution with 0.01% SDS. This washing process was repeated for a total of five times.

Control experiments were done by charging the as-obtained microgels coated with Au with or without Au–S bond into a buffer solution containing 0.01 M PBS, 0.01% SDS and 0.01 M NaCl, and then NaCl was gradually added until the concentration reached 0.7 M, the mixture was incubated at room temperature for 12 h. The as-prepared samples were characterized by TEM (JEOL, JEM 2100) and SEM (S-4800, Japan Hitachi, operating voltage of 5.0 kV) with no prior treatment of the samples.