High-Fidelity Fabrication of Au-Polymer Janus Nanoparticles using a Solution Template Approach

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Abstract

Janus particles have attracted significant attention recent years, due to their potential in nanomanufacturing. Their asymmetric features impart unique physical and chemical properties, which can be tuned and utilized to control their solution-state assembly. While several examples have been reported in the literature, the scientific community continues to pursue synthetic routes which are less time and resource intensive. Herein, we describe a facile method to synthesize Janus nanoparticles in which colloidal micelles template the in-situ formation of Au nanoparticles in the shell layer. The resulting morphologies of the hybrid Au-polymer nanoparticles can be adjusted widely by controlling the polymer and reducing agent (HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid)) concentrations. High-fidelity Au-micelle Janus nanoparticles are obtained when the polymer concentration is high (∼1.0 × 10⁻⁷ M/L) and HEPES concentration is low (<0.3 M/L). Conversely, when HEPES concentration is high (∼0.5 M/L) and polymer concentration is low (∼2.4 × 10⁻⁷ M/L), raspberry-like clusters are formed, where each micelle is encumbers several Au nanocrystals. Our method is attractive in that the number of Au nanoparticles on each Au-micelle entity can be controlled using a scalable, aqueous solution process. It also has significant potential for the directed assembly of Au nanoparticle superstructures, as the nature and geometry of the polymer precursors can be varied.

General Procedure

Scheme 1. Schematic illustration of the process to generating Au-micelle asymmetric nanoparticles

Self-Assembly of Block Copolymer

Figure 1. (a) Bright field TEM image of PEO-b-PS micelles; (b) Hydrodynamic radius, Dₜₐ, measured by dynamic light scattering show a nearly monodisperse micelle population with the average size measuring 40 nm

Figure 2. (a) Statistical histogram of Au-Micelle Janus nanoparticle occupation under different reaction conditions. The overall portion is changing with HEPES and micelles concentrations; (b) Bright field TEM images of Janus nanoparticles; (c) Bright field TEM images of raspberry-like Au-Micelle hybrid, of which each micelle has multiple Au nanoparticles.

Characteristic Surface Plasmon Resonance (SPR)

Figure 3. (a) Change of average peak wavelength of Au nanocrystals in Au-micelle hybrid with micelle and HEPES concentrations. Points with different colors lying on the solid and dash lines have the corresponding full UV-vis spectra in (b); (b) Eight full UV-vis spectra curves according to the peak wavelength lying in solid and dash lines in (a), which clearly show the blue-shift of dash lines from the corresponding solid lines

Conclusion

Morphologies of Au-micelle nanoparticles can be changed from Janus structure to raspberry-like structure. This strategy will help broaden existing “bottom-up” fabrication strategies

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