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Asymmetric functionalization of colloidal dimer particles with gold nanoparticles†

Kisun Yoon,^a Daeyeon Lee,^b Jin Woong Kim,^c Jaeyun Kim^{ad} and David A. Weitz^{*a}

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We present a method to asymmetrically functionalize dimer particles with gold nanoparticles. Our method enables the fabrication of asymmetrically functionalized dimer particles on a large scale.

Dimer particles are a new class of colloids made of two partially fused spherical lobes. Dimer particles with high uniformity in size and shape can be produced in a large quantity (~grams) using seeded-emulsion polymerization.^{1–3} These dimer particles have been used as building blocks to fabricate new photonic materials, and other complex structures.^{4–9} They have also been studied as colloid surfactants for the stabilization of pickering emulsions.¹⁰ To fully take advantage of the anisotropy of dimer particles, it is highly desirable to develop methods to tailor the surface property of each lobe independently. The asymmetric functionalization of dimer particles would expand their application as colloid surfactants, since the shape and surface anisotropies can be controlled independently, analogous to molecular surfactants such as diblock copolymers. The asymmetric surface functionalization of dimer particles, however, has not been explored extensively. It has been shown that only one lobe of dimer particles can be further functionalized.^{1,10} Other studies have shown that asymmetric functionalization of spherical colloids can be achieved by the selective deposition of a metal (*e.g.* gold) onto one hemisphere of particles.^{11–14} These approaches, however, require two-dimensional arrangement of particles at an interface, which is difficult to achieve with dimer particles.^{15–17}

In this work, we present a novel method to synthesize asymmetric gold-coated submicron dimer particles. Selective deposition of gold nanoparticles on one lobe of the dimers is

achieved in solution by simply mixing the dimer particles with gold nanoparticles. The two lobes of these asymmetrically gold-coated dimer particles have distinct functional groups, which can be further modified to have various pairs of anisotropic surface properties. Our method does not require the arrangement of particles at interfaces for asymmetric functionalization, thus, can be used to generate uniform anisotropic particles on a large scale. In addition, the attachment of nanoparticles can endow unique functionality such as plasmonic and magnetic properties to the dimer particles.

The synthesis of the asymmetric gold-coated dimer particles proceeds in four steps. Surfactant-free emulsion polymerization is followed by two sequential seeded-emulsion polymerization, and, subsequently, by the selective attachment of gold nanoparticles to one lobe of dimer particles (Fig. 1).^{2,3,10,18} We use surfactant-free emulsion polymerization to synthesize monodisperse linear polystyrene (LPS) particles.^{19,20} These particles serve as the seeds for the first seeded-emulsion polymerization (Fig. 2(a)). Linear polystyrene particles are stabilized by surface sulfate groups generated from a water soluble radical initiator, potassium persulfate.^{19–21} The average diameter of the LPS particles is ~380 nm. In the first seeded-emulsion polymerization, the LPS particles are mixed with an oil-in-water (O/W) emulsion, where the oil phase is styrene, 2,2'-azodi(2,4'-dimethylvaleronitrile) (ADVN; initiator) and 3-(trimethoxysilyl) propyl acrylate (TMSPA). The TMSPA contains an acrylate group, which copolymerizes with styrene. The TMSPA also contains tri-alkoxy silane, which provides reactive sites to enable further functionalization.¹⁰ Upon mixing the LPS dispersion with the monomer emulsion, monomers diffuse into LPS particles and form monodisperse droplets. These swollen LPS droplets are converted to TMSPA-functionalized LPS particles by raising the temperature of the mixture to 70 °C for 24 h (Fig. 2(b)). The second seeded-emulsion polymerization is performed to obtain dimer particles. The TMSPA functionalized LPS dispersion is mixed with an O/W emulsion. The oil phase of this emulsion contains styrene and ADVN but does not contain TMSPA. Upon mixing with the O/W emulsion, spherical TMSPA-functionalized LPS particles

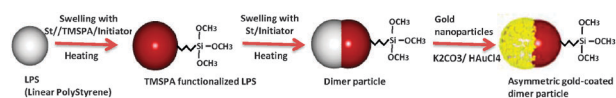


Fig. 1 Schematic illustration showing the synthesis of dimer particles with asymmetric coating of gold nanoparticles.

^a School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA.
E-mail: weitz@seas.harvard.edu; Fax: +1 617 495 0427;
Tel: +1 617 496 2842

^b Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, 19104, USA

^c Department of Applied Chemistry, Hanyang University, 55 Hanyangdaehak-ro, Sangnok-gu, Ansan, Gyeonggi-do, 426791, Republic of Korea

^d School of Chemical Engineering, Sungkyunkwan University, Suwon, 440746, Republic of Korea

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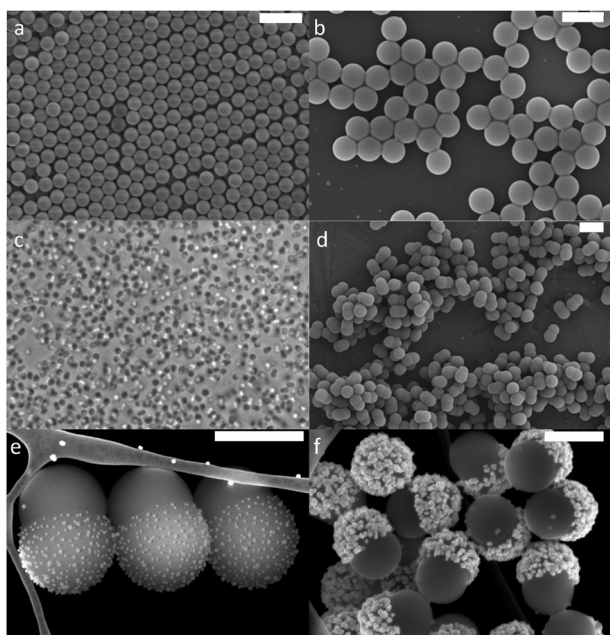


Fig. 2 (a) SEM image of seed particles obtained by surfactant emulsion polymerization. The scale bar represents 1 μm . (b) SEM image of TMSPA functionalized LPS. (c) Optical microscope image (100 \times) of dimer particles right after swelling of the monomer mixture. (d) SEM image of dimer particles. The scale bar represents 1 μm . (e) Submicron dimer particles with asymmetric gold coating. The scale bar represents 500 nm. (f) Dimer particles with asymmetric gold coating after growth of gold nanoparticles. The scale bar represents 500 nm.

spontaneously transform into a dimeric structure (Fig. 2(c)). The shape and size of the dimeric structure is highly uniform. These dimeric structures have been reported to form from a core-shell structure obtained from the seeded-emulsion polymerization.³ Styrene and LPS form the core which phase separates from the hydrophilic shell made of TMSPA-rich polystyrene copolymers. Polymerization to solidify the dimeric structure is initiated by raising the temperature to 70 $^{\circ}\text{C}$ for 24 h (Fig. 2(d)). The addition of citrate-stabilized gold nanoparticles leads to the formation of asymmetrically gold-coated dimer particles as seen in Fig. 2(e).²² Ultrasonication does not detach the gold nanoparticles from the dimer particles, indicating that the adhesion between the two particles is strong. The size of gold nanoparticles on the dimers can be further increased by adding potassium carbonate-chloroauric acid solution and hydroxylamine hydrochloride solution to the dimer particle dispersion (Fig. 2(f)). Gold ions selectively adsorb onto pre-existing gold nanoparticles and are reduced. The formation of larger gold nanoparticles is evident from the change in the color of dispersion from wine red to dark violet. The size of the gold nanoparticles can be controlled by adjusting the amount of potassium carbonate-chloroauric acid solution.

To verify which lobe of the dimer particles has affinity to citrate-stabilized gold nanoparticles, we test the interactions of two types of particles with citrate-stabilized gold nanoparticles: seeded emulsion-polymerized particles with and without TMSPA. Gold nanoparticles do not show affinity to

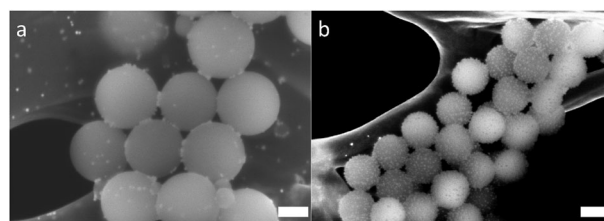


Fig. 3 (a) SEM image of seeded emulsion polymerized particles with TMSPA after deposition of gold nanoparticles. The particles do not have affinity to gold nanoparticles. The scale bar represents 200 nm. (b) Seeded emulsion-polymerized particles without TMSPA. The particles show affinity to gold nanoparticles. The scale bar represents 300 nm.

particles with TMSPA, whereas gold nanoparticles adsorb favorably onto particles without TMSPA as shown in Fig. 3. The TMSPA likely undergoes hydrolysis during the synthesis, making the surface of the particles similar to that of silica particles.²³ It is known that citrate-stabilized gold nanoparticles do not adsorb favorably onto the silica surface due to electrostatic repulsions.²⁴ We hypothesize that the binding of gold nanoparticles onto particles without TMSPA is driven by non-electrostatic forces such as van der Waals interaction and hydrophobic interactions between the hydrophobic polystyrene surfaces and the gold nanoparticles.

Our hypothesis is further supported by the formation of dimer particles that are fully coated with gold nanoparticles (Fig. 4(a)). We functionalize dimer particles with amine groups using an amino-silane-coupling agent, *N*-[3-(trimethoxysilyl)propyl] ethyleneamine (TMSPE). The TMSPE reacts with TMSPA to impart amine groups onto the particle surface.¹⁰ This reaction, therefore, selectively converts the TMSPA-functionalized surface to an amine-functionalized surface. TMSPE-functionalized dimer particles are subsequently mixed with citrate-stabilized gold nanoparticles. The resulting dimer particles have uniform coatings of gold nanoparticles on both sides of the dimers as seen in Fig. 4(b). Attractive interactions between amine groups and citrate-stabilized gold nanoparticles through electrostatic interactions are well known and widely exploited to induce the adsorption of gold nanoparticles onto silica surfaces.²⁵ Thus this result clearly indicates that the lobe that did not have affinity to gold nanoparticles contains TMSPA.

The method presented in this work can be extended to generate dimer particles that are asymmetrically coated with other types of nanomaterials. For example, by mixing dimer particles with gold nanorods²⁶ or iron oxide nanoparticles,²⁷

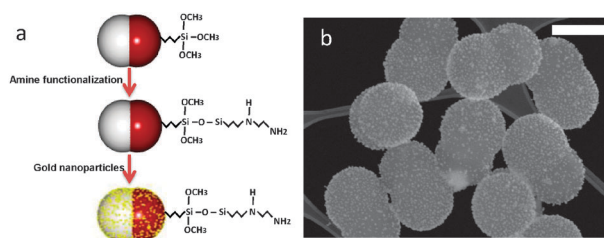


Fig. 4 (a) Schematic representation of the synthesis of amine functionalized dimer particles with gold nanoparticles. (b) SEM image of amine functionalized dimer particles with gold nanoparticles. The scale bar represents 500 nm.

asymmetrically functionalized dimers are obtained (see ESI†). These results illustrate that our method provides a general approach to selectively adsorb nanoparticles onto one lobe of the dimer particles.

In this communication, we have presented a method to asymmetrically functionalize dimer particles with nanoparticles. This solution-based batch synthetic approach has advantages compared to other asymmetric functionalization methods because it does not require the use of vacuum-based metal deposition. Our method enables the fabrication of asymmetrically functionalized dimer particles on a large scale. The partitioning of TMSPA in one lobe and the selective adsorption of gold nanoparticles onto the other lobe provide new opportunities to independently control the surface properties of these dimer particles. The lobe with gold nanoparticles can be functionalized with a variety of well-known thiols,²⁸ whereas the other lobe can be further functionalized using silanes.²⁹ Therefore, these asymmetrically functionalized dimer particles represent promising building blocks to generate suprastructures that will be useful in photonic, electronic and diagnostic applications.^{30,31}

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