



Thermo-responsiveness and tunable optical properties of asymmetric polystyrene/PNIPAM-gold composite particles



Mingmeng Zhang^a, Noelle I. Rabiah^a, Thao H. Ngo^a, Todd P. Otanicar^b, Patrick E. Phelan^a, Raja Swaminathan^a, Lenore L. Dai^{a,*}

^aSchool for Engineering of Matter, Transport, and Energy, Arizona State University, Tempe, AZ 85281, USA

^bDepartment of Mechanical Engineering, University of Tulsa, Tulsa, OK 74104, USA

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ABSTRACT

Environmentally responsive polystyrene/poly (N-isopropylacrylamide)-gold composite particles are successfully synthesized via a Pickering emulsion polymerization method. It is found that the core-shell and asymmetric structured particles are simultaneously formed during the polymerization. Compared with the core-shell structured composite particles, the asymmetric particles have a higher thermo-responsiveness as a result of differences in morphology and formation mechanism. For asymmetric composite particles, an increase in N-isopropylacrylamide (NIPAAm) content leads to more significant size variation upon temperature changes. From rheology measurements, the viscosity of asymmetric particles suspension greatly decreases as temperature is increased above the lower critical solution temperature (LCST). The large size decrease in asymmetric composite particles gives rise to a significant scattering intensity increase, as a result of increased refractive index contrast between the PNIPAM content and surrounding water. The resulting size decrease also leads to tunable surface plasmon resonance properties.

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Introduction

The synergistic combination of “smart” polymers and inorganic nanomaterials is attracting increasing interest in recent years. In response to temperature [1–6], or pH [7–9], the stimuli-responsive polymers are able to smartly adjust nanomaterial's optical [1–4], catalytic [5,6] and transport properties [7,8]. In particular, poly (N-isopropylacrylamide) (PNIPAM) is a water-based gel and compatible with many biological systems. Its unique thermo-responsiveness enables the gel to undergo a sharp volume phase transition at lower critical solution temperature (LCST) [10]. Gold nanoparticles (AuNPs) are well-known for their strong surface plasmon resonance (SPR) properties, which arise from collective resonance oscillation of electrons in the conduction band [11], and lead to a range of applications in optical sensing [12,13]. Several PNIPAM-gold composite materials have been synthesized with unique structure, showing that the material's optical properties can be tuned based on PNIPAM's thermo-responsiveness. For example, Lange et al. investigate PNIPAM-gold composite particles with two different structures (AuNPs cover the PNIPAM microgel core and AuNPs are included inside the PNIPAM microgel). They

demonstrate that by increasing the temperature above LCST, the particles undergo size decrease, with SPR band red-shifting as a result of decreased interparticle distance [14]. Tagliazucchi et al. present a model demonstrating that for PNIPAM-coated AuNPs, as the coated PNIPAM layer collapses above the LCST, the change in refractive index of the PNIPAM medium leads to a slight red-shift of the particle's SPR wavelength [1]. Sorrell et al. fabricate a color-tunable film in which the PNIPAM microgel layer is sandwiched by two Au substrates. The color-tunable property is based on tuned interference properties [4,15].

Conventional methods of synthesizing polymer-gold core-shell particles are mainly based on chemical binding (e.g. utilizing thiol [16]/amine group [17]) or electrostatic attraction interaction [18] and often require multiple procedures. In this work, we apply a one-step Pickering emulsion polymerization route with the original objective to synthesize core-shell polystyrene/PNIPAM-gold composite particles, where the AuNPs serve as the emulsion stabilizer and subsequently form the shell. In the Pickering emulsion method, the emulsions are stabilized by AuNPs, driven by thermodynamic requirement [19]. In addition to the formation of core-shell structured composite particles, an intriguing observation is that asymmetric particles (a single AuNP coats on each polystyrene/PNIPAM substrate particle) are formed simultaneously (see Fig 1). A recent study of polymer-inorganic asymmetric

* Corresponding author.

E-mail address: Lenore.Dai@asu.edu (L.L. Dai).

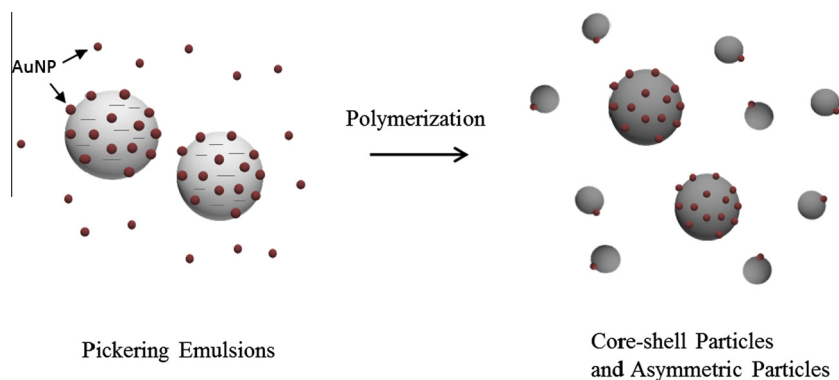


Fig. 1. Scheme of core-shell and asymmetric polystyrene/PNIPAM-gold composite particles formation.

particles is performed by Ohnuma et al., where the precipitation polymerization method is applied to synthesize polystyrene-gold asymmetric particles [20]. In our work, the PNIPAM polymer is incorporated into the Pickering emulsion route to validate the thermal responsiveness of the asymmetric composite particles. Another novelty of this work is that the asymmetric gold-PNIPAM particles are synthesized without cross linker, compared with traditional gold-PNIPAM particles synthesized with the aid of cross-linking agent [2,21,22]. More importantly, the asymmetric particles synthesized in the absence of cross linker show a much more significant particle size and viscosity variations around the LCST.

For gold-PNIPAM particles, investigations have mainly focused on adjusting the SPR absorption properties of AuNPs via tuning the inter-particle distance [3,5,14] and refractive index of the AuNP's surrounding medium [1,2,22]. However, tuning or utilizing the particle's scattering intensity remains less-explored. Light intensity is a key factor for optical devices and could be utilized as signals for intensity-based optical sensors, which is potentially the simplest optical sensor [23]. For example, particles with switchable scattering intensity could be utilized in thermal sensor, in which the thermo-responsive scattering intensity serves as signals. Aslan et al. developed a wavelength-ratiometric resonance light scattering technique for glucose sensing based on AuNPs aggregation and dissociation. Instead of absorption signals, the plasmon resonance scattering signals of AuNPs are analyzed for glucose sensing [24]. In addition, the switchable light intensity properties provide potential applications in photo-catalytic reactions, considering light intensity is an important factor for such reactions [25,26] Here we demonstrate that significant thermo-responsiveness of scattering intensity is achieved for asymmetric polystyrene/PNIPAM-gold composite particles, based on the large temperature-dependent shrinking/swelling of the polystyrene/PNIPAM core. In addition, the tunable SPR absorption properties of asymmetric polystyrene/PNIPAM-gold composite particles are also discussed.

Methodology

Materials

Spherical AuNPs, (20 nm, wt% of 3.0%, capping agent Nsol (alkyl acrylate), Nanopartz Inc.), styrene monomer (99.9%, Fisher), N-isopropylacrylamide monomer (NIPAAM, 97%, Aldrich), nonionic initiator VA-086 (98%, 2,2-azobis(2-methyl-N-(2-hydroxyethyl) propionamide), Wako Chemicals), and water (HPLC grade, Acros Organics) are utilized in the Pickering emulsion polymerization process without further purification. *N,N'*-methylene-bis-acrylamide (MBA) (MP Biomedical LLC.) is used as cross linker.

Particle synthesis

Typically, 0.05 g AuNPs dispersion, 15 ml water, a varying amount of styrene (0.1–0.5 g), a varying amount of NIPAAM (0.05–0.5 g) are sonicated by a VCX 500 ultrasound sonicator to form the emulsion. The emulsion is then immediately transferred to a 3-neck 15 ml flask and degassed with nitrogen for 15 min. After the solution is heated to 65 °C, 0.028 g VA-086 initiator in 0.3 ml water solution is injected. The reaction lasts for 3 h. The core-shell and asymmetric particles are separated by centrifugation with speed of 5000 rpm for 20 min. The core-shell particles settle down after centrifugation; the pure asymmetric particles are collected from the upper solution. Before characterization, the synthesized sample is washed with water by three centrifugation-redispersion cycles to remove unreacted monomers/oligomers and unattached AuNPs. For the control experiment with cross linkers, 5% (mole percentage) of MBA is added with styrene and NIPAAM monomers.

Characterization techniques

Particle size distributions of the polystyrene/PNIPAM-gold composite particles are obtained by NICOMP 380 ZLS with dynamic light scattering (DLS) technique. The transmission electron microscopy (TEM) images are obtained via an environmental TEM Tecnai F20. The TEM specimen is prepared by placing one droplet of the solution onto TEM grids and air-drying the specimen. The energy-dispersive X-ray spectroscopy (EDX) spectra are obtained by utilizing a Philips CM-200 FEG TEM's adjunct X-ray detector. An AR-G2 rheometer is used to measure the viscosity of solutions of asymmetric particles under steady-state flow procedure, where a 25 mm plate-plate geometry is used. The UV-Vis extinction properties of the sample are analyzed via a Cary 300 Bio UV-Vis spectrophotometer. The temperature control function is utilized to study the temperature transition property of NIPAAM-incorporated particles. Extinction intensity data are taken from a Cary 300 Bio UV-Vis spectrophotometer with a laser wavelength of 639 nm. Scattering intensity data are taken from the NICOMP 380 DLS machine with laser wavelength of 639 nm.

Results and discussion

Bimodal size distribution of polystyrene/PNIPAM-gold composite particles

We successfully synthesize polystyrene/PNIPAM-gold composite particles with a bimodal size distribution. Fig. 2a is the TEM images of core-shell structured and asymmetric composite

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