



Facile synthesis of gold/polymer nanocomposite particles using polymeric amine-based particles as dual reductants and templates



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ABSTRACT

Herein we report a facile synthesis of gold nanoparticle/polymer nanocomposite particles through a spontaneous reduction of tetrachloroauric (III) acid and encapsulation of resultant gold nanoparticles using amine-rich polymeric particles in water. The particle consisted of core–shell nanostructure with a dense layer of polyethyleneimine (PEI) shell. The hydrophilic PEI shell acted as a reductant to generate gold nanoparticles (AuNPs), while the particle as a polymer template to *in-situ* encapsulate and stabilize the resultant AuNPs, giving a stable gold/polymer nanocomposite particle in water. The PEI-based core–shell particles with different degree of softness were found to have little influence on the reduction ability of the gold salt, but considerably affect the encapsulating capability. Increasing the level of softness of particle core gave higher encapsulation efficiency to the gold nanoparticles. A soft type of core–shell microgel, namely poly(*N*-isopropyl acrylamide)/polyethyleneimine (PNIPAm/PEI) was further investigated with respect to the reduction rate, encapsulation efficiency, as well as nanocomposite stability and properties. Results indicated that reduction rate of gold salts using the PNIPAm/PEI microgels as the reductant was two orders of magnitude faster than that of the native PEI. Solution pH and amine to gold salt ratio also affected the formation of Au@PNIPAm/PEI composite particles. Our results demonstrate that the use of polymeric amine-based particles is a simple and green synthesis of Au@polymer nanocomposite particles in aqueous system which is free from organic solvent, reducing and stabilizing agents.

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1. Introduction

Gold/polymeric composite particles have attracted much research interests because of their synergistic effects of the gold nanoparticles on optical and electronic properties, biological compatibility and nano-scale size, as well as the polymer which enables the control of the composite particles through inducing chemical and physical changes of the polymer and surface functionality. The combined chemical and physical properties of the gold/polymer composite particles have opened up many potential applications in various emerging fields including sensing [1,2], biomedicine [3,4], and catalysis [5]. The gold/polymer composite particles can be synthesized using different types of polymers such

as homopolymer [6], block copolymers [7–9], and colloidal particles [10–14]. Among the various polymer mediated synthesis, amphiphilic particles with polyelectrolyte brushes are of particular interest because the hydrophilic brush shells can act as both nanoreactors and templates for gold nanoparticle formation and *in-situ* encapsulation of the resultant metallic nanoparticles. Lu et al. have reported a type of core–shell particle composing of a solid polystyrene core grafted with long cationic polyelectrolyte chains of poly(2-aminoethyl methacrylate hydrochloride) (PAEMH) [15,16]. When dispersing such type of particles in water, the polyelectrolyte shells become highly swollen, giving dense layer of polymer chains on the particle surface. Their counterions could reside within the shell layer of the core–shell particles. When $[\text{AuCl}_4]^-$ ions are added into the particle dispersion, they could undergo metal ion exchange with the counterions, resulting in confining the negatively charged gold ions within the cationic brush-like shells. This type of colloidal particles was synthesized via first producing a hydrophobic core, e.g. polystyrene (PS)

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through a conventional emulsion polymerization, followed by attaching the photo initiator on the surface of the core. The water-soluble macromonomer was then polymerized from the surface of the core to form tree-like structures. However, such method of producing gold/polymer composite particles can be tedious and expensive. They also need to use stabilizer as well as toxic and highly reactive reducing agents to generate gold nanoparticles. These drawbacks would limit many potential applications of the gold/polymer composite particles. Recently, Agrawal et al. reported a reducing agent free synthesis of gold nanoparticles using poly(*N*-vinyl caprolactam-co-acetoacetoxyethyl methacrylate-co-acrylic acid) P(VCL-AAEM-AAc) microgels as the template [17]. Gold nanoparticles were confined within the core region of the template particles. It was speculated that β -diketone groups of AAEM located in the core was responsible for the reduction of gold salt to nanoparticles due to its electron rich atoms from keto-enol tautomerization.

Amines are a particularly attractive class of compounds because of their almost universal presence in many biological and environmental systems. Amine-containing polyelectrolytes have been reported to act as dual reductants and stabilizers in gold nanoparticle synthesis [18–23]. Mechanistic studies suggest that tertiary amines are most effective in reducing Au^{3+} , while secondary amines are more effective in providing the necessary coordination for stabilizing gold nanoparticles as they are formed. Primary amines can form quaternary ammonium sites in water, thus capable of attracting negative gold salt precursors through electrostatic interaction [24]. Apart from functioning as reductant and source of binding sites, polymeric amines can also act as capping agent to limit the growth and agglomeration of the metallic nanoparticles. Furthermore, polymeric amines are pH-sensitive, thus inter-particle distance between those immobilized gold nanoparticles can be altered through varying solution pH, giving different optical property and morphology of the nanocomposite particles. Among various types of polymeric amines, branched polyethyleneimine (PEI), a cationic polymer comprising 25, 50 and 25% primary, secondary and tertiary groups, respectively, has received much attention in the past two decades because it is one of the most potent non-viral polymeric vectors for gene delivery [25]. Our group has already synthesized a variety of PEI-based core-shell particles and studied their formation mechanism [26–28]. We have also developed diverse applications using these core-shell particles because of their unique chemical and physical properties such as high surface area to volume ratio, well-defined core-shell nanostructure with tunable composition, surface functionality, and good water dispersibility [29,30].

As part of our continuous development in core-shell particle platform technology, we envision that the amine-rich core-shell particles could act as multifunctional polymer particles for gold nanoparticle synthesis and spontaneous immobilization. Thus the gold/polymer composite particles could be generated in the absence of any toxic reducing and stabilizing agents. Therefore, this work aimed at using PEI-based core-shell particles as a green and efficient platform for generating gold/polymer composite particles in water. The core-shell particles in this system play dual functions: as nanoreactor and reductant to generate AuNPs, and as a polymer template to spontaneously encapsulate and stabilize the resulting AuNPs, forming stable gold/polymer composite particles in an aqueous.

2. Experimental section

2.1. Materials

Branched poly(ethyleneimine) (PEI) (50% solution in water with

a weight average molecular weight of 750,000), *N,N*-methylenebisacrylamide (MBA) and *tert*-butyl hydroperoxide (TBHP, 70% solution in water) were all purchased from Sigma Aldrich Chemical Co., and used without further purification. Methyl methacrylate (MMA, Aldrich) was purified by washing it three times with 10% sodium hydroxide solution (volume ratio of MMA to NaOH solution was 10: 1), followed by repeated washing with deionized water (volume ratio of MMA to water was 5: 1) until the pH of the aqueous phase dropped to neutral. Spindle-crystals of *N*-isopropylacrylamide (NIPAm, Aldrich) were purified by repeated recrystallization of the NIPAm monomer using a mixture of toluene and *n*-hexane (1:5 v/v). Hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was purchased from Aldrich–Sigma and used as received. Deionized water or Milli-Q water was used for dilution and dispersion medium.

2.2. Synthesis of gold/polymer composite particles

Three types of PEI-based particles were used to prepare Au-loaded composite particles through a simple mixing with hydrogen tetrachloroaurate(III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) solution according to the following general procedure: Hydrogen tetrachloroaurate (III) trihydrate stock solution (1.317×10^{-3} M) was purged with N_2 for 30 min. This gold salt solution (1 mL) was added dropwise into the PNIPAm/PEI microgel dispersion (20 mL, 400 ppm, molar ratio of N/Au³⁺ was 28). The mixture was stirred at 250 rpm for 4 h at 25 °C. Kinetic experiments were carried out for 96 h to monitor the reduction rate profile of the gold ions with either PEI or PEI-based microgels with the same PEI content. The resultant gold-loaded microgels were purified by a single cycle of centrifugation at 12,000 rpm for 1 h at 10 °C. The suspended pink product was redispersed into deionized water under sonication. A similar procedure was used for other types of PEI-based particles such as PMMA/PEI core-shell particles and PEI-g-PMMA hollow particles using amine to Au³⁺ molar ratios of 19:1 and 30:1, respectively.

2.3. Measurement and characterization

2.3.1. Particle size and surface charge measurement

The hydrodynamic diameter and zeta-potential of the template particles and gold-loaded composite particles were determined with a Beckman Coulter Delsa Nanoparticle analyzer using a photon correlation spectroscopy with electrophoretic dynamic light scattering (a two-laser diode light source with a wavelength of 658 nm at 30 mW). Hydrodynamic diameter, D_h , was obtained from the Einstein Stokes equation, $D_h = kT/3\pi\eta D$, where k is the Boltzmann constant, η is the dispersant viscosity, T is the temperature (K), and D is the diffusion coefficient obtained from the decay rate of the intensity correlation function of the scattered light (i.e., correlogram), $G(\tau) = \int I(t)I(t + \tau)dt$. Surface charges of particles were measured based on their electrophoretic mobility. Samples for zeta-potential measurement were diluted to 100–200 ppm with 1 mM NaCl solution and measured at 25 °C. Each value was an average of triplicate measurement.

2.3.2. Scanning electron microscopy

Scanning electron microscope (SEM) samples were examined with a JEOL-JSM 6335 field emission scanning electron microscope at an accelerating voltage of 5 kV. A diluted sample (around 200 ppm) was spread onto a glass substrate, followed by air-dried in a covered, free-dust environment. A thin layer of gold film with 2–5 nm thickness was sputtered on the dried sample under vacuum.

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