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Facile control of the self-assembly of gold nanoparticles by changing the capping agent structures

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HIGHLIGHTS

- The assembly process of gold nanoparticles is controlled by surfactant structures.
- The distribution fashion of capping agent is the key factor for the gold nanochains.
- Systems with mixed nonionic surfactants were further investigated.
- The different capping fashions transform gold nanochains into single nanoparticles.
- The diverse capping fashions interpret the different stabilities of nanostructures.

GRAPHICAL ABSTRACT
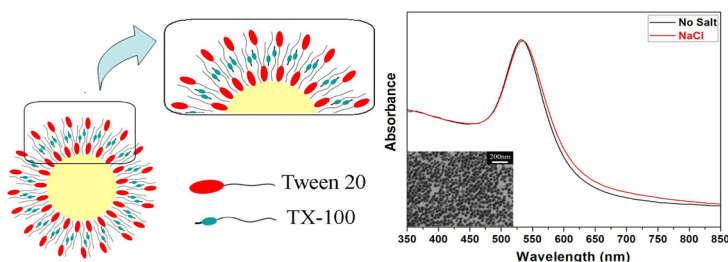
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ABSTRACT

Facile synthesis and 1D self-assembly of gold nanoparticles were achieved using a series of nonionic surfactants (Tween 20, Tween 40, and Tween 60). The assembly process can be controlled by adjusting the fine structures of surfactants. The effects of the molecular structures of capping agents were demonstrated and the formation mechanism based on the nonuniform distribution of capping ligands around gold nanoparticles was proposed. Systems with mixed capping agents (Tween 20 and Tween 60 or Triton X-100) were also investigated. Due to the different capping fashions of the mixed surfactants, the obtained gold nanostructures were changed from chains to particles. Besides, the diverse capping fashions can also interpret the different stabilities of the nanostructures in the saline solutions.

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1. Introduction

In the past decade, gold nanoparticles have stimulated tremendous research interest owing to their promising applications in many fields [1,2]. The 1D assembly of gold nanoparticles with well-defined structure is crucial for the fabrication of next-generation optoelectronic devices due to their unique, coherent optical properties [3]. Several experimental routes have been recently proposed to efficiently assemble preformed gold nanoparticles, involving hard, polymeric or surfactant-based templates, molecular recognition, specific functionalization, and biorecognition systems [3–10]. For example, Xu et al. employed cationic conjugated polymers to prepare gold nanochains by the assembly of citrate-stabilized gold nanospheres [7]. Recently, Nergiz et al. demonstrated large and reversible tuning of plasmonic properties of gold

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nanoparticles mediated by the reversible breaking and making of linear and branched chains of gold nanoparticles adsorbed on an ultrathin responsive polymer film [8]. The driving forces of 1D self-assembly, such as the electrostatic interaction, hydrogen bond and so on, were fully discussed and demonstrated [6–10]. However, the assembled process and mechanism remain mostly under-investigated and thus poorly controlled, which is the major limitation for their effective applications.

To better understand the mechanism and dynamics of the growth reaction during the self-assembly, more attention should be paid to the precise control of the assembled degree and the ability to track the assembly at different stages of the process. There have been several initial attempts to investigate the assembled dynamics [11–16]. Dujardin et al. investigated the mechanism of gold nanoparticle chain assembly associated with the induction of electric dipole–dipole interactions. They provided a general mechanistic model for the self-assembly of metallic nanoparticles based on ligand-induced electric dipolar interactions [11,12]. Recently, Singamaneni et al. demonstrated that the assembly process could be terminated immediately at a desired stage of the process by using competitive ligands to interact with either the cross-linker or gold surface. This technique is named "double ligand competitive binding" [13]. Besides the use of crosslinking molecules, the assembly of gold nanoparticles was also controlled by the addition of destabilizing species (e.g., salt) to the nanoparticle aqueous dispersion [14–16]. The chain-like assemblies could disassemble upon dilution of the salt or the evaporation of ethanol if the gold nanoparticles were protected with a sufficiently strong ligand [16]. More recently, Yin et al. studied the thermo-responsive assembly and disassembly of colloidal gold nanoparticles in aqueous solution and demonstrated the reversible tuning of Plasmon coupling by controlling the temperature of the colloidal dispersion [17]. Although the above methods can control the assembly process of gold nanoparticles, the main approaches are to change the external conditions, such as the temperature, the additional capping agents and so on, which may bring some dicey effects to the whole systems. So we attempt to find a facile strategy to achieve the same effects by controlling the fine structures of the capping agents.

Various surfactants, with different head groups, hydrophobic chains, counterions, and molecular architectures, have been widely employed as capping or inducing agents to control the nucleation, growth and assembly of gold nanocrystals. Particularly, the cationic surfactants of quaternary ammonium salts are most frequently used for the synthesis of gold nanostructures in aqueous solution [18]. Then, other cationic surfactants, such as amphiphilic ionic liquid, fluorocarbon surfactant, and fluorocarbon–hydrocarbon hybrid surfactant were also used in the fabrication of gold nanocrystals [19–23]. Besides, due to the synergistic interactions of the binary surfactants, the mixed surfactants have also been used as binary capping agents for the controlled synthesis of gold nanocrystals [24,25]. In general, due to the electrostatic interaction with the gold nanoparticles, the ionic surfactants have been employed for the controlled synthesis of gold nanocrystals. But the use of nonionic surfactant as the capping agent has been seldom reported. The nonionic surfactants are more stable and less sensitive for salinity and pH value of the aqueous solution. Recently, our group used a nonionic siloxane surfactant for the mild synthesis and simultaneous 1D assembly of gold nanoparticles [26]. The multiple functional groups of the surfactant molecule play the key role in the formation of gold nanochains. Then, we further reported a facile, green, and high yield approach for the synthesis and stabilization of relatively monodispersed gold nanoparticles using typical non-ionic biosurfactant ethoxylated sterol (BPS-30) [27]. The obtained gold nanoparticles capped by BPS-30 showed remarkable stability in the high concentrations of electrolyte aqueous solutions. Therefore, we consider that it is necessary to investigate the exact roles of the molecular structures of the capping agents in detail.

In this work, we present our latest efforts to prepare the assemblies of gold nanoparticles capped by nonionic surfactants. The mixed capping agents were also used to stabilize the gold nanostructures. The results reveal that the molecular structures, especially the hydrophobic chains of the capping agents strongly affect the assembled degree of gold nanoparticles.

2. Experimental

2.1. Chemicals

Tween 20, Tween 40, Tween 60 (Fig. S1) and $HAuCl_4$ was purchased from Shanghai Chemical Reagent Co. Triton X-100 (TX-100) (Fig. S2) was obtained from Alfa Aesar Ltd. and evaporated under vacuum at 80 °C for 4 h to remove the excess water. All other chemicals were analytical grade and used as received.

2.2. Synthesis

In a typical synthesis, 0.25 mL of Tween 20 (5 mM) and 0.25 mL of $HAuCl_4$ (10 mM) solutions were added to 4.4 mL of water at room temperature. Then, 0.1 mL of ascorbic acid solution (0.1 M) was added, and the final concentrations of Tween 20, $HAuCl_4$, and ascorbic acid were 0.25, 0.5, and 2.0 mM, respectively. The mixture was kept unstirred for 24 h. The obtained gold nanochains were collected by centrifugation, washed thoroughly with deionized water. The concentration and kind of surfactants were varied to examine its effects on the synthesis of gold nanostructures.

2.3. Characterization

The gold nanostructures were characterized by transmission electron microscopy (TEM) (JEM-100CX II (JEOL)) and UV–vis spectroscopy (Hitachi U-4100). X-ray diffraction (XRD, Rigaku D/max-rA) was conducted with Cu $K\alpha$ radiation (40 kV, 40 mA, 8°/min) and 2-theta range of 30–90°.

3. Results and discussion

3.1. Single capping agent systems

It has been reported that many conditions during preparation will affect the final assembled structures, and the concentration is one of the most important factors [22]. Fig. 1 shows the TEM images of samples prepared under different Tween 20 concentrations. At low concentration of Tween 20 (0.25 mM), the nanochains, consisted of hundreds of gold nanoparticles, are more than several micrometers in length and one nanoparticle width (about 20 nm) (Fig. 1a). The bifurcated junctions with outgrowths are often interconnected to produce an extended branched network. However, the length of the assemblies decreased with the increase of the concentration (Fig. 1a–c). When 0.5 mM Tween 20 is added, the aggregated sample mainly consists of short linear nanochains with lengths of 75–150 nm (Fig. 1b), equivalent to 5–10 isomeric 20 nm gold nanoparticles. When the concentration of Tween 20 is increased to 1.0 mM, dimers, trimers, or oligomers of nanoparticles, instead of short nanochains, are formed in solution, as shown in Fig. 1c. The assembly of linear nanostructures is hindered completely in the presence of a vast excess of Tween 20 (2.0 mM), and the particles are dispersed rather uniformly in solution without any orderly arrangement than induced chainlike aggregation (Fig. 1d). Interestingly, the mean diameter of individual gold nanoparticles is almost unchanged with different Tween 20 concentrations.