Preparation and Characterization of Nano-Sized Silver Particles

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Abstract

This study presents an approach to prepare nano-sized silver particles via in-situ reduction process. First, a reversible addition fragmentation chain transfer (RAFT) agent, 2-(dodecylthiocarbonothioylthio)propanoic acid (DTPA), was synthesized and characterized. Acrylic acid (AA) was polymerized in the presence of DTPA to afford an amphiphilic macro RAFT agent (DTPA-AC-10) with a calculated average degree of polymerization of ten. Latex particles with a sodium salt-containing shell were prepared by using sodium DTPA-AC-10 as a reactive surfactant. Then, through silver ion-exchange processs of the latex particles, the latex particles with silver salt at the surface were obtained. Finally, the silver salt at the particle surface was reduced through chemical reduction to give the silver-coated polymer particles. Dynamic Laser Scattering (DLS) was used to measure the particle size and distribution; X ray diffraction analysis (XRD) was employed to characterize the formed silver crystal in the particle surface. The diameter of the silver particles was about 76 nm and was narrowly distributed. The silver nanoparticles might be used to prepare conductive ink for ink-jet applications.

Introduction

The nano-sized silver particle have the particular properties of surface, optics, chemistry, electricity and so on. In recent years, people pay much attention to the nano-sized silver particle. It has a growing scope of applications in the field of electronic industry [1-3], biology antibacterial [4,5], conductive ink-jet ink [6], etc. There are a number of ways for preparing nano-sized silver particles [7-16], among which a commonly used approach is the chemical reduction of silver salt. Silver salt can be dispersed in water in the form of the micro-emulsion with the help of stabilizer or surfactant. The silver ions of the micro-emulsion are reduced to gain the nano-sized silver particle. However, the size of the particle and stability of the emulsion depend on the kind of stabilizer or surfactant, the pH value and other factors [171. In this study, we synthesized a reactive macromolecular surfactant which was used to prepare the latex particle with a chemically bonded ionic shell through soapless emulsion polymerization. Then through silver ion exchange process, silver ion was transferred onto the surface of the particles. The silver salt at the particle surface was finally reduced by chemical reduction to get the silver-coated polymer particles. DLS was used to measure the particle size and distribution; XRD was employed to characterize the formed silver crystal in the particle surface.

Experimental

Materials and Methods

Butyl methacrylate (BMA), acrylic acid (AA), dodecane-1-thiol, 2-bromopropanoic acid, 4,4'-azobis (4-cyanovaleric acid) (ACVA), silver nitrite and ascorbic acid were commercial products from Beijing Chemicals Co. BMA were purified by vacuum distillation before use. De-ionized water was used in all the experiments.

The average particle size and distribution were measured by dynamic light scattering (DLS) with a Dynapro Titan instrument (Wyatt, American). X-ray diffraction (XRD) analysis was performed on a D/MAX-RD diffractometer with Cu Ka radiation.

Synthesis and Characterization of DTPA and DTPA-AC-10

In a 250-mL, four-necked flask equipped with a mechanical stirrer and a reflux condenser was placed 8.00 g (0.20 mmol)of sodium hydroxide, 40 ml of deionized water. The mixture was stirred and cooled to room temperature. Tetraethylammonium bromide (3.20g, 0.01mol), THF (40 ml) and dodecane-1-thiol (40.48 g, 0.20 mol) were added to the mixture and stirred to yield a clear solution. Then, 15.23 g of CS_2 (0.20 mol) and subsequently 30.6 g of 2-bromopropanoic acid (0.20 mol) were added to the above solution in such a way that the temperature could be kept at 20-25 ^oC. The mixture was stirred at room temperature for 20 h and then at 50 ^oC for another 5 h. After cooling to room temperature, the yellowish organic layer was separated and poured into an excess amount of petroleum ether with stirring to yield a yellow precipitate. The yellow product was recrystallized in methanol to give 57.5 g of DTPA. Yield: 82%. mp: 64-65 ^oC. FTIR (KBr, cm^{-1}): 2918, 2852, 1701, 1421, 1209, 1084, 825. ^1H NMR (300MHz, $CDCl_3$): 4.82-4.90 (m, 1H), 3.32-3.38 (m, 2H), 1.66-1.74(m, 2H), 1.60-1.64 (d, 3H), 1.25-1.38 (m, 18H), 0.84-0.87 (m, 3H). ESI (m/e, percentage of relative intensity): 349. ELEM. ANAL. Calcd. For $C_{16}H_{30}O_2S_3$: C, 54.81; H, 8.62; S, 27.44. Found: C, 54.56%; H, 8.74%; S, 27.67%.

DTPA-AC-10 was prepared according to a reported procedure [18]. In a typical experiment, DTPA (3.5g, 0.01mol), AA (7.2 g, 0.05 mol), ACVA (0.29g, 1.03 mmol) and toluene (20 ml) were charged in a 100 ml flask, which was then flushed with nitrogen for 1 h. The temperature was raised to 60 °C and stirred for 8 h. The solution became viscous and additional 5 ml of toluene was added. The reaction solution was cooled to room temperature and then poured into 100 ml of petroleum ether. The yellowish precipitate was collected and fully washed with petroleum ether and dried in vacuo at 50 °C to afford 9.8 g (Yield: 92%) of DTPA. FTIR (film, cm^{-1})：3330-3400，2920, 2850, 1706, 1420, 1210, 1088, 830. Number-average molecular weight (*M*n): 1036; weight-average molecular weight (*M*w): 1595; polydispersity index (PI): 1.54.

Synthesis of polymer latex particles with the ionic shell

The macro RAFT agent (DTPA-AC-10) sodium salt, was used as reactive surfactant to prepare poly(butyl methacrylate (PBMA) particles with the ionic shell. 0.60 g of DTPA-AC-10, 0.08 g of ACVA initiator and 0.25 g of sodium hydroxide was

dissolved in 15 ml of water. Then 11.40 g of BMA was added. The stirred mixture was purged with nitrogen for 1 h. The mixture was heated in an oil bath at 60 °C and kept for 6 h. The resulted emulsion had a solid content of the about 44.7 wt.%.

Preparation of Latex particles with the silver coated surface

Aqueous solution of 0.74 g of silver nitrate (10 wt.%) was prepared and was added dropwise to the above emulsion under constant stirring. After the addition, the mixture was stirred for 6 h. Then, the solution of 1.08 g of ascorbic acid in 10 ml water was added dropwise to the emulsion and stirred for 24 h. The emulsion gradually became black from white.

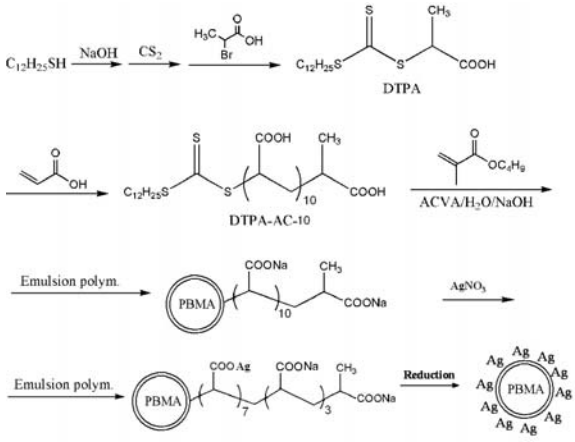
Results and Discussion

Preparation of the RAFT agent, DTPA-AC-10 and the latex particles coated with silver

The synthetic route of DTPA, DTPA-AC-10 and the latex particle were depicted in Scheme 1. The RAFT agent, DTPA, was obtained in high yield. The structures of the compound were confirmed by elemental analysis, IR, ^{1}H NMR and MS. The polymerization of AA was carried out in the presence of one-tenth the molar concentration of RAFT agent in toluene (Scheme 1) to give a macro RAFT agent. The resulting product, (AA)x-RAFT, was characterized by Gel permeation chromatography (GPC) (relative to styrene standards). The value of M_n measured by GPC is 1036, which is close to the calculated value of DTPA-AC-10 (M_n= 1070). The PI value is 1.54, which is less than those observed for polymers prepared through traditional radical polymerization (typically greater than 2). All these indicate that DTPA-mediated polymerization of AA is characterized by "live" radical polymerization. The obtained macro RAFT agent should have a polymerization degree of about ten.

Emulsion polymerization of BMA was conducted using the sodium salt of DTPA-AC-10 as surfactant. DTPA-AC-10 was a reactive surfactant for it also took part in emulsion polymerization and became part of the formed particle. Furthermore, the hydrophilic moieties of DTPA-AC-10, namely the sodium carboxylate groups, were located at the surface of the latex particles, providing a stable hydrophilic layer around the surface which stabilized the emulsion.

Ion exchange reaction between silver nitrite and the sodium carboxylate surface group of the PMBA latex particle occurred when the silver nitrite solution was added to the emulsion. It should be noted that the silver nitrite solution should be added slowly to avoid possible precipitation of the emulsion. The molar ratio of silver nitrite to sodium salt was 7:10, hence the calculated conversion of the sodium carboxylate to the corresponding silver carboxylate should be 70 %. In-situ reduction reaction of silver carboxylate readily took place in the presence of ascorbic acid, resulting in nano-sized particles covered with a thin silver shell. The size of the particles was determined with the help of DLS (Figure 1), and it was found that the particles were found narrowly distributed in size (polydispersity 5%) and the mean diameter was 76 nm (Figure 1). As shown in Figure 2, the color of the latex turned from milky white to dark black, indicting the generation of silver. According to the experimental section, the percent silver of the solid particle was less than 3.7%.



Scheme 1. *Synthesis of DTPA, DTPA-AC-10 and latex particles coated with silver*

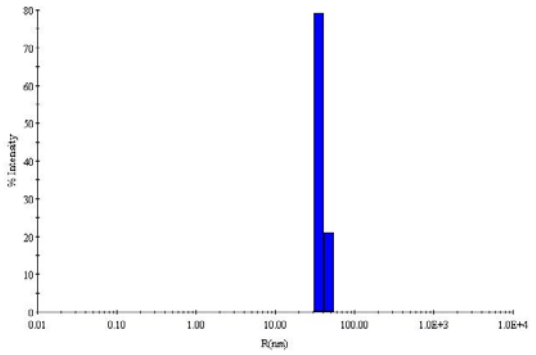


Figure 1. *Dynamic Laser Scattering (DLS) analysis of the latex particles covered with silver*

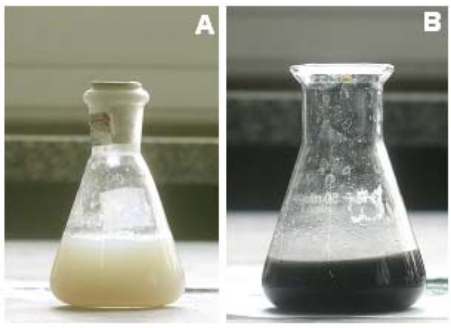


Figure 2. *Photographs of the latex after Ion exchange reaction with silver nitrite solution (A) and reduction by ascorbic acid (B)*

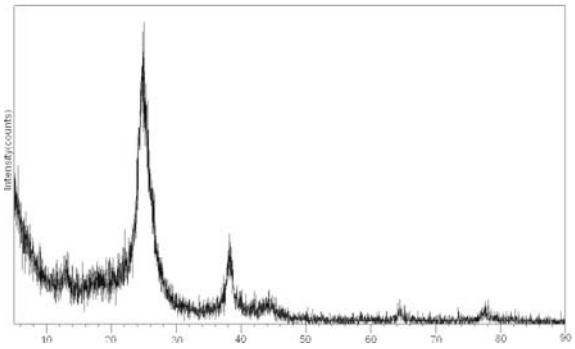


Figure 3. *XRD pattern of the silver-coated latex particle*

X-ray diffraction (XRD) analysis of the Latex Particles

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of materials. The obtained nanoparticle was characterized by XRD to show the presence of crystalline silver. Figure 3 shows the typical XRD patterns of the prepared sample. Four peaks located at 38.1°, 44.3°, 64.4° and 77.3° can be found, which are indexed to diffraction from the (111), (200), (220) and (311) of face-centered cubic (fcc) Ag (JCPDS No. 420783). However, X-ray diffraction peak broadening caused by dislocations is observed, showing that the particles are smaller [19].

Conclusion

In this study, a simple but effective route for the synthesis of well-defined, narrowly distributed silver-coated latex particle was described. Though the prepared nanoparticle has lower silver content (less than 4%), however, it should be similar to those prepared by general methods in many in many aspects such as antibiotics, optical, catalytic or even electronic properties because the properties of nano-sized particles depend on the surface structures. Investigations of the physicochemical properties and potential applications of the silver-covered particles are in progress.

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Author Biography

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