Ag Nanocomposite Particles: Preparation, Characterization and Application

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Summary Herein, we report that different core-shell particles could be successfully used as the carrier systems for the deposition of silver nanoparticles. Firstly, thermosensitive core-shell microgel particles have been used as the carrier system for the deposition of Ag nanoparticles, in which the core consists of poly (styrene) (PS) whereas the shell consists of poly (N-isopropylacrylamide) (PNIPA) network cross-linked by N, N′-methylenebisacrylamide (BIS). Immersed in water the shell of these particles is swollen. Heating the suspension above 32 °C leads to a volume transition within the shell, which is followed by a marked shrinking of the network of the shell. Secondly, "nano-tree" type polymer brush can be used as "nanoreactor" for the generation of silver nanoparticles also. This kind of carrier particles consists of a solid core of PS onto which bottlebrush chains synthesized by the macromonomer poly (ethylene glycol) methacrylate (PEGMA) are affixed by "grafting from" technique. Thirdly, silver nanoparticles can be in-situ immobilized onto polystyrene (PS) core-polyacrylic acid (PAA) polyelectrolyte brush particles by UV irradiation. Monodisperse Ag nanoparticles with diameter of 8.5 nm, 7.5 nm and 3 nm can be deposited into thermosensitive microgels, "nano-tree" type polymer brushes and polyelectrolyte brush particles, respectively. Moreover, obtained silver nano-composites show different catalytic activity for the catalytic reduction of *p*-nitrophenol depending on the carrier system used for preparation.

Keywords: Ag nanoparticles; catalytic activity; core-shell

Introduction

In recent years, the immobilization of metal nanoparticles[1] in a polymeric matrix such as dendrimers, latex particles, microgels, or other polymers,[2–4] has fascinated scientists because of the importance such systems may have in nanotechnology. The metal nanoparticles exhibit the size-induced quantum effects, and have possible applications as sensor, and in electronics and catalysis.[5] In principle, suitable carrier systems may be used as a "nanoreactor", in which the metal nanoparticles can be immobilized and used for the purpose at hand. Thus, Crook's group[2,6] reported that dendrimers can act as both templates and porous nanoreactors and the dendrimer-encapsulated noble metal clusters show highly catalytic activity. More recently, Kumacheva and co-workers[7,8] introduced polymer microgels as carrier systems for nanoparticle.

Silver nanoparticles are particularly interesting due to their roles as substrates in studies of surface-enhanced Raman scattering, fluorescence, and catalysis.[9–10] Oxidation and aggregation of Ag nanoparticles, however, prevented further applications up to now. For preparation of Ag particles, Ag ions are often reduced in the protective colloids by addition of reducing agents such as sodium borohydride.[11] In photochemical reduction, hydrated electrons or free

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organic radicals formed by γ-rays or UV light can also reduce metal ions to metals.[12–13]

In this paper, we reported that different core-shell particles have been used as the carrier systems for the deposition of silver nanoparticles either by chemical reduction or by UV irradiation. Firstly, thermosensitive core-shell microgel particles have been used as the carrier system for the deposition of Ag nanoparticles, in which the core consists of poly (styrene) (PS) whereas the shell consists of poly (N-isopropylacrylamide) (PNIPA) network crosslinked by N, N′-methylenebisacrylamide (BIS).[14–15] Secondly, "nano-tree" type polymer brush can be used as "nanoreactor" for the generation of silver nanoparticles also. This kind of carrier particles consists of a solid core of PS onto which bottlebrush chains synthesized by the macromonomer poly (ethylene glycol) methacrylate (PEGMA) are affixed by "grafting from" technique.[16–17] Thirdly, silver nanoparticles can be in-situ immobilized onto polystyrene (PS) core-polyacrylic acid (PAA) polyelectrolyte brush particles by UV irradiation. The synthesis of these composite particles proceeds through a photo-emulsion polymerization in aqueous dispersion using the functional monomer silver acrylate.[18–19] In this way the layer of the chains of poly(acrylic acid) on the surface and the Ag-nanoparticles are formed at the same time. Moreover, the catalytic activity of silver nanocomposites is investigated using the reduction reaction of 4-nitrophenol by sodium borohydride.[9,20] Here we shall demonstrate that the Ag-composite particles present stable catalysts.

Preparation of Ag Nanocomposite Particles

Firstly, thermosensitive PS-NIPA core-shell particles have been used as the template, which allows us to modulate the activity of nanoparticles by a thermodynamic transition that takes place within the carrier system.[14,15] The principle is shown in Figure 1: Metallic nanoparticles are embedded in a polymeric network attached to a colloidal core particle. In all cases to be discussed here the core consists of poly(styrene) (PS) whereas the network consists of poly(N-isopropylacrylamide) (PNIPA) crosslinked by N, N′-methylene-bisacrylamide (BIS). The particles are suspended in water that swells the PNIPA at room temperature. The PNIPA-network, however, undergoes a volume transition around 32 °C in which most of the water is expelled. Hence, the process of shrinking and re-swelling can be repeated without degradation or coagulation of the particles.

Secondly, a new type of colloidal spherical polymer brush system synthesized by photo-emulsionpolymerization of the macromonomer poly (ethylene glycol) methacrylate (PEGMA) may be also used as well-defined nanoreactors for the

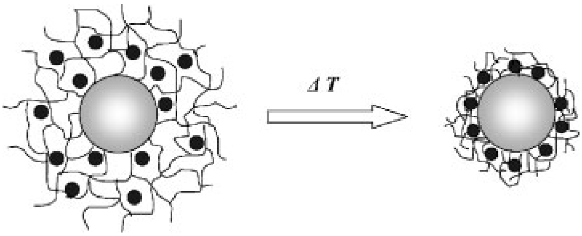

Figure 1.
Schematic representation of PS-NIPA-Ag composite particles consisting of thermosensitive core-shell particles in which metallic nanoparticles (here: Ag) are embedded. The composite particles are suspended in water, which swells the thermosensitive network attached to the surface of the core particles. In this state the reagents can diffuse freely to the nanoparticles that act as catalysts. At higher temperatures ($T > 30$ °C) the network shrinks and the catalytic activity of the nanoparticles is strongly diminished in this state.

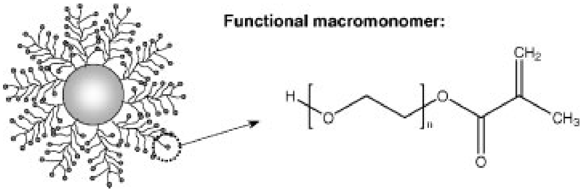

Figure 2.
Model for the "Nano tree" type PS-PEGMA brushes prepared by the macromonomer of hydroxy poly(ethylene glycol) methacrylate (PEGMA) ($n = 13$).

generation of silver nanoparticles. The bottlebrush chains are affixed to colloidal poly(styrene) sphere by a "grafting from" technique.[18] Figure 2 shows the structure of these particles in a schematic fashion. The surface of colloidal core particles is covered by highly branched polymer chains. Hence, a "Nano tree"-type morphology can be achieved for the brush layer attached to the core particles.

Thirdly, silver nanoparticles are in-situ formed on the surface of PS-PAA brush particles by choosing functional monomer silver acrylate as the water-soluble monomer for the photo-polymerization (see Figure 3). In principle, the radicals formed by photolysis of the HMEM groups on the PS core surface will start the radical polymerization of the shell. Under UV irradiation acrylic monomer will form the

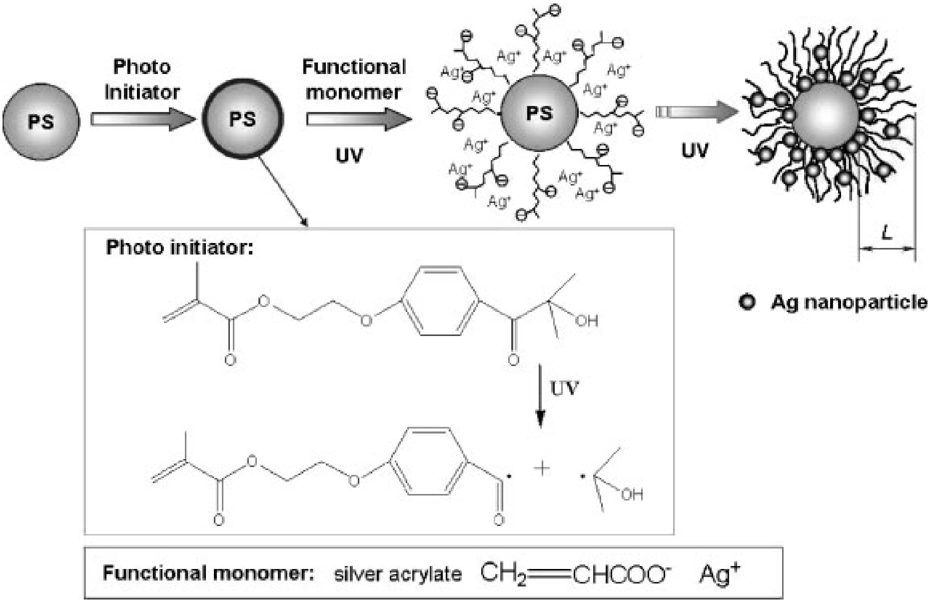

Figure 3.
Schematic representation of the preparation of PS-PAA-Ag composite particles in-situ. Poly(styrene) (PS) core particles are first prepared by a conventional emulsion polymerization. In a second step, the PS-cores are covered with a thin layer of photo-initiator HMEM. In the third step, the shell of polyelectrolyte brushes is formed by photo-emulsion polymerization: Shining light on the aqueous suspension of these particles generates radicals at their surface which initiate the radical polymerization of the functional monomer (silver acrylate) on the surface of the core particles. Concomitantly the silver anions embedded in the PAA brushes are reduced into Ag nanoparticles under UV irradiation.

polyelectrolyte brushes affixed onto the PS core surface. The new feature is that the Ag^+ counterions of the acrylic acid will be reduced at the same time by the radicals to yield metallic Ag. In this way the local concentration of Ag^+-ions will be kept low which is expected to reduce the size of the Ag-nanoparticles.

As demonstrated in previous studies, cryogenic transmission electron microscopy (cryo-TEM) is the method of choice to investigate the morphology of such composite particles in situ, that is, in aqueous phase.[21,22] The morphology of obtained silver composite particles has been studied by this method and compared with the Ag nanoparticles, which were prepared by using different core-shell particles as the template (as shown in Figure 4). When thermosensitive PS-NIPA particles are used as the template, it is shown in Figure 4(left) that the dark spherical area indicates the PS core whereas the light corona around the dark core is the PNIPA shell of the particles. The Ag nanoparticles are seen as the small black dots. And it is evident that most of the silver nanoparticles are immobilized inside the PNIPA-networks affixed to the surface of the core particles. In Figure 4(middle) dark spherical area indicates the PS cores whereas the light lines affixed on the dark core are PEGMA brushes. It is shown that silver nanoparticles are homogeneously embedded into the spherical PS-PEGMA brushes. Figure 4(right) displays the cryo-TEM image for PS-PAA-Ag nano-composites. It is shown that small black silver nanoparticles are all located on the spherical PS-PAA brush particle surface, which is accord with the morphology of the cationic polyelectrolyte brush-metal composite particles obtained previously.[23–24] In all cases, no metal particles can be observed outside of the template particles, which indicates that Ag nanoparticles can be effectively immobilized by all these three types of core-shell particles. Monodisperse Ag nanoparticles with diameter of 8.5 nm, 7.5 nm and 3 nm can be immobilized into thermosensitive microgels, "nano-tree" type polymer brushes and polyelectrolyte brush particles, respectively.

Catalytic Reduction of 4-Nitrophenol

The catalytic activity of silver nanocomposites has been also investigated for the reduction reaction of 4-nitrophenol by sodium borohydride, which is a benchmark reaction for monitoring the catalytic activity of metal nanoparticles. Figure 5(left) demonstrates that the rate constants k obtained at different temperatures for Ag nano-composites prepared by thermosensitive PS-NIPA particles do not follow the typical Arrhenius-type dependence on temperature, which is due to the volume transition of PNIPA-network. This demonstrated that the catalytic activity of the Ag

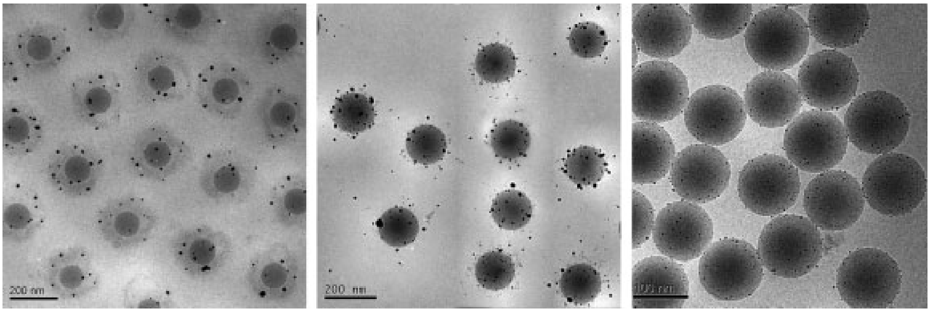

Figure 4.
Cryo-TEM images for PS-NIPA-Ag composite particles (left), PS-PEGMA-Ag particles (middle) and PS-PAA-Ag composite particles (right), respectively.

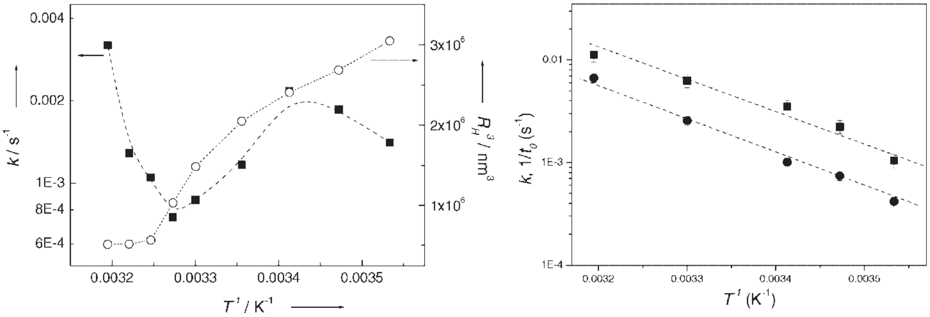

Figure 5.

Arrhenius plot of the reaction rate $k(T)$ measured in presence of PS-NIPA-Ag (left) composite particles and PS-PEGMA-Ag (right)(Quadrangles) composite particles at different temperatures. The circles give the reciprocal delay time $1/t_0$. The concentrations of the reactants are: [PS-NIPA-Ag] = 6.3*10^{-3} g/l, [PS-PEGMA-Ag] = 4.56*10^{-3} g/l, [4-nitrophenol] = 0.1 mmol/l, [NaBH$_4$] = 10 mmol/l.

nanoparticles immobilized within the thermosensitive carrier particles can be modulated over one order of magnitude by the volume transition of the carrier system. While for the PS-PEGMA-Ag composite particles, typical Arrhenius-type dependence on temperature has been found for the rate constants k_{app} obtained at different temperatures as shown in Figure 5(right).

A strictly linear relation between k_{app} and the surface of the metal nanoparticles can be observed in Figure 6. From Figure 6, it can be demonstrates that Pt and Pd nanoparticles exhibit higher catalytic activity than Ag nanoparticles, which may be due to the different kinetic barriers of the reaction for different metal particles. Moreover, it is interesting to note that the catalytic activity of Ag nanoparticles immobilized in the polyelectrolyte brush system is higher than that of the microgel system. This can be explained by the diffusion speed of reactant molecules to metal nanoparticles encapsulated in both carrier systems. For the microgel system, the metal nanoparticles are immobilized in the cross-linked PNIIPA shell, thus reactant molecules need a longer time to reach catalytic active center. While in the case of polyelectrolyte system that has an open structure, reactant molecules can diffuse in latex particles and reach metal nanoparticles more quickly. This demonstrates that spherical polyelectrolyte brush particles can work as stable carrier systems for metal nanoparticles used in catalysis. Similar results have been also observed for Pd composite particles.

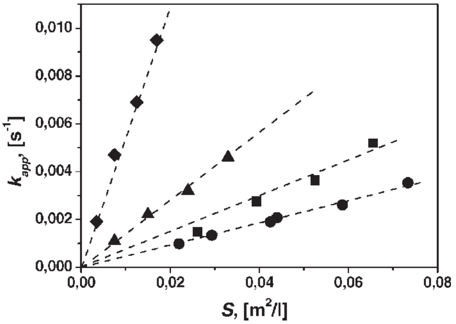

Figure 6.

Rate constant k_{app} as function of the surface area S of metal nanoparticles normalized to the unit volume of the system. Squares: PS-PAA-Ag composite particles; circles: PS-NIPA-Ag composite particles; triangles: PS-NIPA-Pd composite particles [Ref.24]; diamonds: SPB-Pt composite particles [Ref.23].

Conclusions

Different core-shell particles could be successfully used as the carrier systems for the deposition of silver nanoparticles. Monodisperse silver nanoparticles with the diameter in the range of 3 ~ 8.5 nm can be synthesized. Moreover, obtained silver nano-composites show different catalytic activity for the catalytic reduction of *p*-nitrophenol depending on the carrier system used for preparation.

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