

## New Approach for Preparation of Silver–Polystyrene Heterogeneous Nanocomposite by Polyol Process

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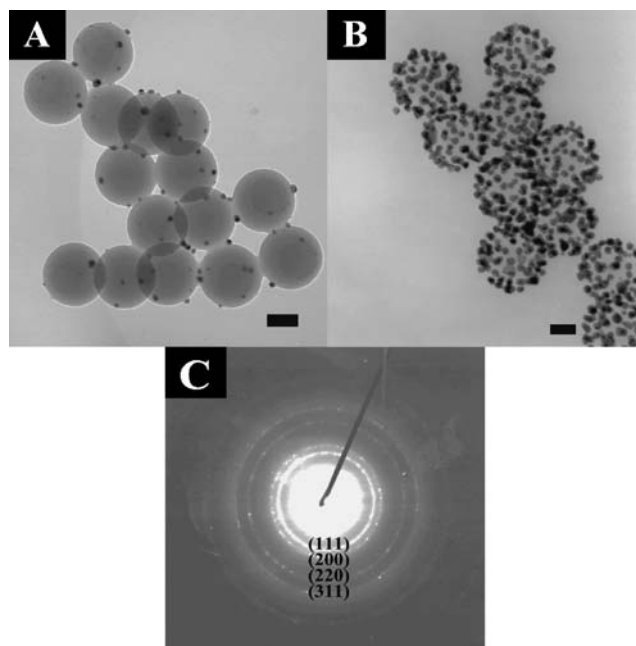
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Silver nanoparticles are homogeneously immobilized onto the polystyrene surface using polyol process for the first time. The formation mechanism of composite materials was discussed briefly. This novel method can be extended to the preparation of other metal–polymer nanocomposites.

Recently, various methods, by which metal nanoparticles are immobilized onto inorganic or organic supports, are developed to expand the application area of nanomaterials and to control the morphology and the behavior.<sup>1</sup> Metal–polymer nanocomposite materials have great advantages over conductivity, mechanical toughness, optical activity, and catalytic activity.<sup>2–5</sup> Moreover, these hybrid materials can prevent metal nanoparticles from agglomerating without the use of a stabilizer and be easily retrieved owing to the relatively large size of polymer supports. As a result, they make it easy to handle metal nanoparticles. But many synthetic routes suffered from complex steps involving preparation of metal colloids and immobilization of metal nanoparticles via covalent interaction or ligand coordination between the protective polymers and supports.<sup>6</sup> Though various methods, using the dispersion copolymerization and the  $\gamma$ -ray irradiation, for the preparation of metal–polymer heterogeneous nanocomposite materials have been investigated to simplify complex reaction process to one-step reaction, it is difficult to obtain sufficiently high coverage yield.<sup>7</sup>

In order to increase the degree of surface coverage, we tried to apply the polyol process,<sup>8</sup> known as a chemical reducing agent free method. To the best of our knowledge, despite the large number of papers published on the polyol process and nanocomposite, the immobilization of silver nanoparticles onto the polymer surface using the polyol process has not been reported yet. In present study, silver nanoparticles, having narrow size distribution, were immobilized onto the polystyrene surface by polyol process for the first time, and the formation mechanism of silver–polystyrene nanocomposite was discussed.

The spherical polystyrene particles were synthesized by emulsifier-free emulsion polymerization technique. Sulfonate groups tend to interact strongly with silver species such as ions, oligomeric clusters, and particles owing to their nucleophilic nature.<sup>9</sup> Using this property, sulfonate groups were used as the chemical protocol to attach the silver nanoparticles to the polystyrene surface. To immobilize the silver nanoparticles onto the polystyrene surface modified with sulfonate group, polyol process was applied. Polyol process is the chemical reduction method using the polyol such as ethylene glycol and diethylene glycol. In this process, polyol acts both as the solvent of the metallic precursor and as the reducing agent. This method seems to be proper for attaching silver nanoparticles to the polystyrene surface because of their low reduction rate compared with direct reduction

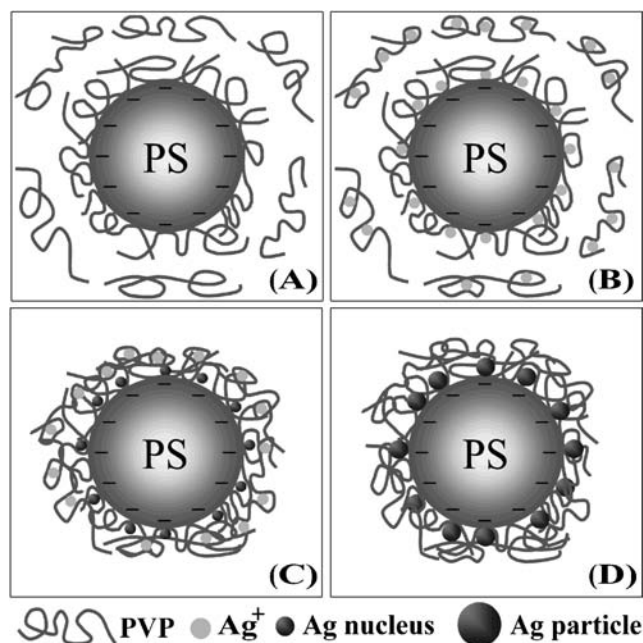


**Figure 1.** TEM images of the silver–polystyrene nanocomposite prepared by polyol process: (A) without PVP and (B) with PVP as a reduction-promoting agent (The scale bars are 100 nm). (C) TEM selected area electron diffraction pattern of silver nanoparticles immobilized onto the polystyrene surface.

method by chemical reducing agent in solution.

In Figure 1A, it can be observed that a small amount of silver nanoparticles is attached to the surface of the polystyrene. This result implies that polystyrene surface acts as a nucleation site. This role of polystyrene surface in silver nanoparticles formation step is similar with that of seed in heterogeneous nucleation technique. Narrow size distribution of individual silver nanoparticles is clear evidence of separation of nucleation and growth step caused by nucleation site role of polystyrene surface. Small amount of silver nanoparticles means that the reduction ability of this system consisting of  $\text{AgNO}_3$ , polystyrene and ethylene glycol is insufficient to reduce  $\text{AgNO}_3$  at a given reaction temperature.

To strengthen the reduction ability of the reaction system, PVP was added into the system. In the polyol process, PVP acts not only as a stabilizer for nanoparticles but also as a nucleation promoting agent.<sup>8</sup> Figure 1B shows the view of TEM photograph of silver nanoparticles immobilized onto the polystyrene surface after reaction in the presence of PVP. In this picture, one can observe that numbers of silver nanoparticles with narrow size distribution are formed and the silver nanoparticles are attached to the polystyrene surface. Also Figure 1C shows the selected



**Scheme 1.** A schematic representation of the formation for the silver-polystyrene nanocomposite by polyol process with PVP.

area electron diffraction (SAED) pattern of resulting material. This suggests that silver nanoparticles on polystyrene surface was crystallized to face-centered cubic (fcc) structure. From above-mentioned facts, it is obvious that PVP molecules successfully promote the formation of silver nanoparticles without interference of formation of combined structure between silver nanoparticles and polystyrene surface. As a result, it can be concluded that silver nanoparticles were formed on the polystyrene surface by nucleation site role of the polystyrene surface (similar role of seeds in the heterogeneous nucleation of polyol technique) and by nucleation promoting agent role of PVP.

Scheme 1 shows the schematic representation of the mechanism for the formation of silver-polystyrene nanocomposite. At the initial stage of the reaction, polystyrene aqueous colloid is added into PVP-ethylene glycol solution (Scheme 1A). PVP molecules are adsorbed on the polystyrene surface by hydrophobic and polar interaction. Hydrophobic interaction occurs between polystyrene surface and hydrophobic methylene/methine groups of PVP, and polar interaction occurs between negative charge of polystyrene surface and positive dipole of the amide nitrogen of PVP.<sup>10</sup> After adding  $\text{AgNO}_3$ , silver ions form complex with sulfonate groups of the polystyrene surface and the excess silver ions form complex with PVP by interaction between the hydrophilic pendant rings of PVP and the silver ions<sup>11</sup> (Scheme 1B). In the presence of  $\text{AgNO}_3$ , interaction between polystyrene and PVP occurs predominantly through the hydrophobic groups, since the polar interactions are screened by the electrolyte present.<sup>12</sup> These adsorption behaviors, silver-sulfonate interaction and PVP-polystyrene interaction, are one of the important reasons why the silver particles are present on the polystyrene surface.

$\text{Ag}^+$  ions are reduced to  $\text{Ag}^0$  metal state by ethylene glycol and PVP, and silver nuclei are formed on the polystyrene surface as the thermal energy is applied to the system by heating to a given temperature (Scheme 1C). Finally, silver nanoparticles

are formed on the polystyrene surface by growth of nuclei<sup>13</sup> (Scheme 1D). Generally, growth of nuclei to metal nanoparticles is accomplished by two mechanisms; one is the deposition of atoms or clusters on the nuclei, and the other is the aggregation of nuclei.<sup>14</sup> In the present case, aggregation is difficult to occur, because silver nuclei are immobilized onto the polystyrene surface. The nucleation site role of  $\text{Ag}^+$  ions bound to sulfonate groups, similar to heterogeneous nucleation, can shorten the reaction time and make it easier to form the metal nanoparticles compared with homogeneous nucleation. In addition, the aggregation proof growth mechanism makes it possible to form silver nanoparticles with narrow size distribution as shown in Figure 1B.

In conclusion, resulting silver-polystyrene heterogeneous nanocomposite particles prepared by present novel method revealed distinguished and outstanding features: high silver particle coverage yield and narrow size distribution of both polystyrene support particles and silver particles. Also, the most distinguished features of this novel preparation route, the polyol process, include simple operation, easy control of metal particles coverage and absence of the toxic reducing agent. In addition, this method can be extended to the preparation of other noble metal-polymer heterogeneous nanocomposites.

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