

양쪽성 가지형 공중합막을 이용한 다양한 모양의 은 나노입자 제조

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Preparation of Silver Nanoparticles with Various Morphology Using Amphiphilic Graft Copolymer Membranes

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요약: Poly(vinyl chloride)-g-poly(styrene sulfonic acid) (PVC-g-PSSA) 가지형 공중합체를 합성한 후, 이를 이용하여 80°C에서 열적으로 환원하여 은 나노입자를 제조하였다. 반응 시간을 바꿈에 따라 다양한 구조의 은 나노입자를 제조하는데 성공하였다. 1시간 정도의 짧은 반응 시간에서는 가지형 공중합체의 미세 상분리 구조를 크게 변화시키지 않고 5 nm 크기의 작은 은 나노입자가 생성되었다. 5시간 정도의 중간 반응 시간에서는 30 내지 50 nm 정도의 크기를 갖는 은 나노입자가 생성되었다. 18시간 정도의 긴 반응 시간에서는, 은입자가 뭉친 허리케인 모양의 은 집합체가 관찰되었다.

Abstract: Silver ions of poly(vinyl chloride)-g-poly(styrene sulfonic acid) (PVC-g-PSSA) graft copolymer were reduced to form silver nanoparticles under thermal condition (80°C). We were successful in synthesizing silver nanoparticles with various morphologies by changing reaction time. At short reaction times (~1 h), silver nanoparticles with 5 nm in size were formed without disrupting a microphase-separated structure of graft copolymer. At medium reaction times (~5 h), silver nanoparticles were aggregated to form large clusters ranging 30~50 nm in size. At much longer reaction times (~18 h), hurricane-like silver clusters were observed due to strong particle aggregation.

Keywords: nanoparticles, morphology, nanomaterials, graft copolymer, silver

1. Introduction

Preparation of nanoparticles, nanocomposites and nano-structured materials has received increased attention recently due to novel properties that are not present at bulk state [1-6]. It has been recognized that the unique properties of nanomaterials originate from their small size and large specific surface area. These materials are considered to be attractive functional materials with wide potential applications such as magnetic resonance

imaging (MRI) [7], electrochemistry [8], and photoluminescence [9]. In particular, interest in silver nanoparticles has increased significantly due to their intriguing optical, electronic, magnetic and mechanical properties [10-17]. Silver nanoparticles have been used as a nanomaterial for antimicrobial activity [18], catalysis [19], surface-enhanced Raman spectroscopy (SERS) [20] and facilitated olefin transport [21].

In this report, we synthesized microphase-separated amphiphilic graft copolymer, i.e. poly(vinyl chloride)-graft-poly(styrene sulfonic acid) (PVC-g-PSSA) via atom transfer radical polymerization (ATRP) and used

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as a template to synthesize silver nanoparticles with various morphologies. Interestingly, silver nanoparticles with various morphologies were synthesized by changing reaction time. The resulting materials were characterized using transmission electron microscopy (TEM) and UV-visible spectroscopy.

2. Experimental

Silver nitrate (AgNO_3 , > 99%), poly(vinyl chloride) (PVC, $M_w \sim 97,000$ g/mol, $M_n \sim 55,000$ g/mol), 4-styrene sulfonic acid (SSA), copper(I) chloride (CuCl , 99%) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 99%) were purchased from Aldrich and used as received without further purification. Amphiphilic PVC-g-PSSA graft copolymer was synthesized via one-step ATRP technique according to the previous method [16]. As-synthesized PVC-g-PSSA with Na^+ form was ion-exchanged with Ag^+ form by immersing AgNO_3 solution. PVC-g-PSSA with Ag^+ form was dissolved in DMSO and stirred at 80°C to allow the reduction reaction [22]. TEM pictures were obtained from a Philips CM30 microscope operating at 300 kV. For TEM measurements, the dried films were dissolved in DMSO, and then a drop of this colloidal solution was placed onto a standard copper grid. UV-visible spectroscopy was measured with spectrophotometer (Hewlett Packard) in the range of 250 to 800 nm.

3. Results and Discussion

The TEM images of PVC-g-PSSA with Na^+ form and silver nanoparticles prepared from PVC-g-PSSA with Ag^+ form at 80°C were shown in Fig. 1. Pristine PVC-g-PSSA with Na^+ form exhibited well-defined microphase separated morphology between PVC main chains and PSSA side chains (Fig. 1(a)). In the Na^+ form, dark regions represent the hydrophobic domains of PVC main chains whereas lighter regions show the PSSA side chains due to high electron density of Cl in PVC. It is thus shown that the amphiphilic PVC-g-PSSA

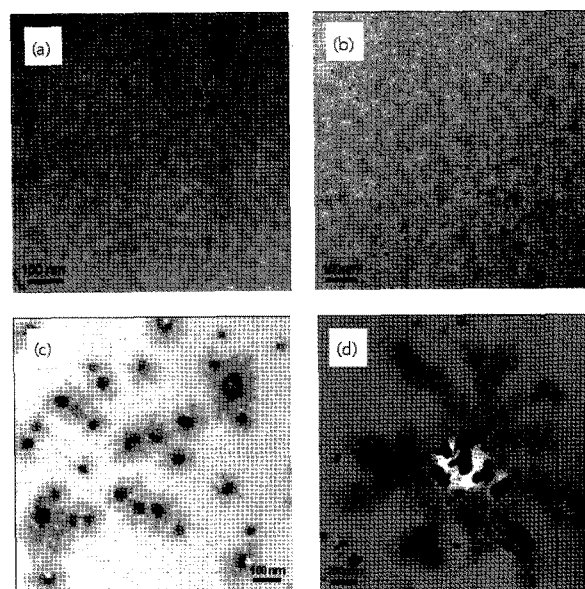


Fig. 1. TEM micrographs of (a) PVC-g-PSSA with Na^+ form, and silver nanoparticles prepared from PVC-g-PSSA with Ag^+ form at 80°C with reaction time; (b) 1 h, (c) 5 h, and (d) 18 h.

graft copolymer self-assemble molecularly into continuous nanophase domains of semicrystalline PVC interweaved with hydrophilic domains of PSSA brush layer. Upon the introduction of Ag^+ and thermal treatment, silver ions were reduced to form silver nanoparticles in PVC-g-PSSA graft copolymer. At short reaction times (~ 1 h), small silver nanoparticles with 5 nm in size were mostly confined in PSSA domains without disrupting a microphase-separated structure of graft copolymer (Fig. 1(b)). When the reaction time was increased to 5 h, silver nanoparticles were aggregated to form large silver clusters ranging 30–50 nm in size (Fig. 1(c)). At much longer reaction times (~ 18 h), hurricane-like silver clusters were observed due to strong particle aggregation. The formation of silver nanoparticles with different morphologies was schematically illustrated in Scheme 1 depending on the reaction temperature.

UV-visible absorption spectra are known to be quite sensitive to the formation of silver nanoparticles [10–21]. Fig. 2 shows the UV-visible absorption spectra for as-synthesized PVC-g-PSSA with Na^+ form and PVC-

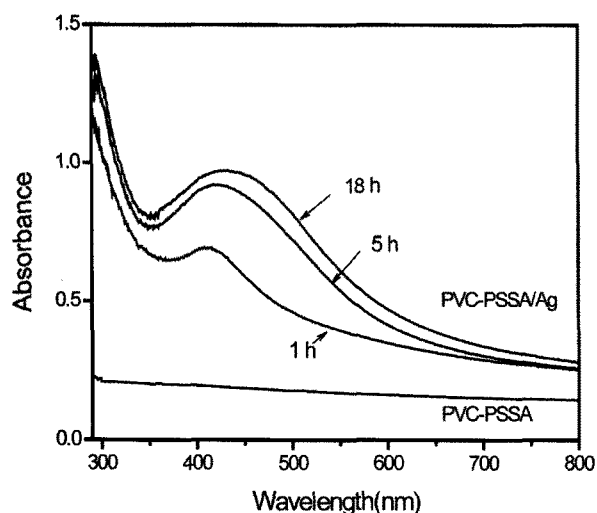
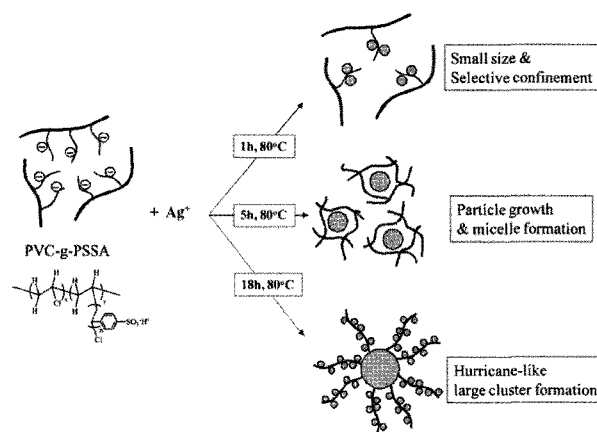


Fig. 2. UV-visible absorption of PVC-g-PSSA with Na^+ form, and silver nanoparticles prepared from PVC-g-PSSA with Ag^+ form at 80°C with different reaction time.

g-PSSA/Ag nanoparticles with different reaction times. In the Na^+ form without reduction process, there was no distinguishable UV absorption for PVC-g-PSSA graft copolymer. Upon ion exchange with Ag^+ and subsequent reduction process, one strong UV absorption peak centered at 412 nm was observed, corresponding to the plasmon excitation of Ag nanoparticles. It is generally accepted that the absorption peak whose maximum occurs at around 410~420 nm is related to the formation of silver metal nanoparticles [10-17]. When reaction time was increased, the maximum peak position shifted to higher wavelength and the peaks became broad, indicating the growth of silver nanoparticles, which is consistent with TEM results.

4. Conclusion

This work has demonstrated that silver nanoparticles with various morphologies were successfully prepared using amphiphilic graft copolymer template upon controlling reduction times. When the reaction time was short (~ 1 h), small silver nanoparticles ranging 5 nm in size were generated within the microphase-separated PVC-g-PSSA graft copolymer. As the reaction time increased, silver nanoparticles grew up to form large



Scheme 1. Schematic illustration for the formation of silver nanoparticles with different morphologies depending on the reaction temperature.

metal clusters ranging 30~50 nm in size. When the reaction time was further increased to ~ 18 h, much larger silver clusters with hurricane-like morphology appeared. These various morphology of silver nanoparticles were related to the amphiphilic structure and properties of PVC-g-PSSA graft copolymer.

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