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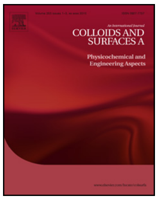

Block copolymer-mediated synthesis of silver nanoparticles from silver ions in aqueous media

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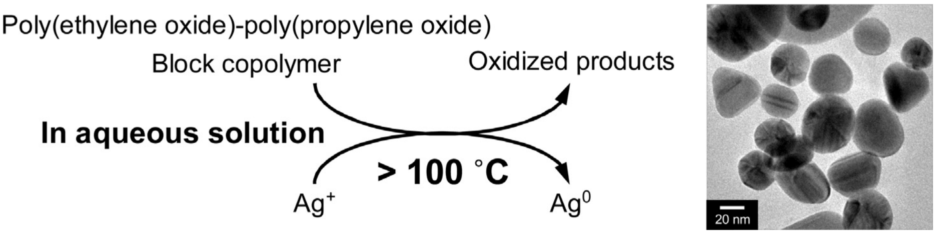
HIGHLIGHTS

- Silver nanoparticles formed from aqueous silver nitrate solutions above 100 °C.
- Reduction of silver ions by poly(ethylene oxide)–poly(propylene oxide) block copolymers.
- Formation of silver nanoparticles enhanced with longer PEO–PPO block copolymers.
- Formation of silver nanoparticles enhanced with higher polymer concentration.

GRAPHICAL ABSTRACT



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ABSTRACT

We report here on the silver (Ag) nanoparticle synthesis in aqueous solutions of poly(ethylene oxide)-poly(propylene oxide) (PEO–PPO) block copolymers in the absence of any additional agents. In particular, we examined the effect of reaction temperature, molecular weight of PEO–PPO block copolymer and PEO–PPO block copolymer concentration on the reduction of silver ions (Ag$^+$) and the resulting formation of Ag nanoparticles in aqueous PEO–PPO block copolymer solutions. We found that Ag nanoparticles were formed from aqueous silver nitrate ($AgNO_3$) solutions containing PEO–PPO block copolymer above 100 °C. This is most likely due to the dehydration of Ag$^+$ caused by thermal motion of water molecules in higher-temperature aqueous solution at high vapor pressure. We also found that the formation of Ag nanoparticles in aqueous PEO–PPO block copolymer solutions was enhanced with larger molecular weight of PEO–PPO block copolymer and with increase in the concentration of PEO–PPO block copolymer in aqueous solutions.

1. Introduction

Nanometer-sized metal particles (metal nanoparticles) are attracting significant attention in the last couple of decades because of their unique properties that are distinct from bulk metal and their wide applications in chemistry, physics and biology fields [1–21]. The physical and chemical properties of metal nanoparticles depend strongly on the size, shape and assembly of metal nanoparticles. Therefore, it is still important and challenging task to develop the controllable synthesis of metal nanoparticles with different sizes, shapes and assemblies. There are a number of reports on the controlling size and shape of metal nanoparticles in wet chemistry.

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Table 1
Properties of the PEO–PPO block copolymers (EOxPOyEO)$_x$ and PEO homopolymer (EO$_x$) used in this study [34].

Pluronic	Molecular weight	PEO wt%	PPO block mol. weight	PEO block mol. weight	cmc (mM) (25 °C)	Nominal formula
P103	4950	30	3465	1485	0.141	$EO_{17}PO_{60}EO_{17}$
F68	8400	80	1680	6720	320.5	$EO_{76}PO_{29}EO_{76}$
F88	11400	80	2280	9120	11.51	$EO_{103}PO_{39}EO_{103}$
F127	12600	70	3780	8820	0.555	$EO_{100}PO_{65}EO_{100}$
F108	14600	80	2920	11680	3.082	$EO_{132}PO_{50}EO_{132}$
PEO	8000	100	0	8000	–	EO_{181}

cmc: critical micellization concentration.

For examine, the size, shape and assembly of gold nanoparticles are controlled by judicious combination of the capping agents (e.g., alkylthiols, surfactants and polymers) and reducing agents (e.g., $NaBH_4$, hydrazine and ascorbic acid). Furthermore, the block copolymer- and supramolecule-mediated synthesis of gold nanoparticles has been developed because the block copolymers and supramolecules can display dual function: the reducing function for metal ions and capping (stabilizing) function for metal nanoparticles formed [22–32]. Silver (Ag) nanoparticles are synthesized through the citrate reduction, silver mirror reaction, polyol process, seed-mediated growth and light-mediated synthesis [19]. We have also developed a facile and efficient synthetic method of gold and silver nanoparticles from reduction of tetrachloroaureate(III) ions ($[AuCl_4]^-$) and silver ions (Ag^+) in solutions of poly(ethylene oxide)–poly(propylene oxide) (PEO–PPO) block copolymers, respectively (named as block copolymer-mediated synthetic method) [33–42]. In this method, gold nanoparticles are formed in both aqueous and formamide solutions of PEO–PPO block copolymers in the temperature range of 4–100 °C. On the other hand, Ag nanoparticles are formed from silver nitrate ($AgNO_3$) formamide solutions of PEO–PPO block copolymer at 100 °C but not from aqueous $AgNO_3$ solutions of PEO–PPO block copolymers at 100 °C for 24 h [37,38]. Then, we explore the synthesis of Ag nanoparticles directly from aqueous $AgNO_3$ solutions of PEO–PPO block copolymers in the absence of any additional agents. The development of synthetic methodology of other metal nanoparticles from gold nanoparticles in aqueous media should provide further opportunities of the block copolymer-mediated synthesis of metal nanoparticles.

In the present work, we examine the effect of reaction temperature, molecular weight of PEO–PPO block copolymer and PEO–PPO block copolymer concentration on the reduction of silver ions (Ag^+) and the resulting formation of Ag nanoparticles in aqueous solutions of PEO–PPO block copolymers. Different from other studies on the Ag nanoparticle synthesis using PEO–PPO block copolymers [43–49], the methodology that we present here aims at the direct synthesis of Ag nanoparticles from Ag^+ in aqueous PEO–PPO block copolymer solutions in the absence of any additives but not from $[Ag(NH_3)_2]^+$ [43–45], not in the lyotropic liquid crystal phase (that is formed in high concentration of PEO–PPO block copolymers) [46] and not in the presence of additives such as reducing agents [47–49].

2. Experimental

2.1. Ag nanoparticle synthesis

Silver (Ag) nanoparticles were prepared by mixing a 20×10^{-3} mol L^{-1} silver nitrate ($AgNO_3$; 99.999+ %, Aldrich) aqueous (18.2 MΩ cm, Millipore-filtered water) solution (0.25 mL) with aqueous solutions (25 mL) containing poly(ethylene oxide)–poly(propylene oxide) (PEO–PPO) block copolymer ($H(OCH_2CH_2)_x(OCH_2(CH_3)CH)_y(OCH_2CH_2)x OH$; Pluronic, BASF Corp.) or poly(ethylene oxide) (PEO) homopolymer ($H(OCH_2CH_2)x OH$; Sigma–Aldrich) in 50 mL container of a Teflon-lined stainless steel autoclave. The PEO–PPO block copolymers that we considered for Ag nanoparticle synthesis in this work are Pluronic P103, Pluronic F68, Pluronic F88, Pluronic F127 and Pluronic F108 [34]. For comparison purposes, a PEO homopolymer (PEG8000, Sigma–Aldrich) was applied for Ag nanoparticle synthesis. Properties of the PEO–PPO block copolymers and a PEO homopolymer considered here are listed in Table 1. The various polymers allow us to examine the effects of metal ion reduction activity (due to block copolymer overall chain length and/or PEO block length) and polymer adsorption, colloidal stabilization (due to block copolymer overall chain length and hydrophobicity) and presence of block copolymer micelles on the formation and structure of Ag nanoparticles. The Ag^+ concentration following mixing (at the start of the reaction) was 2.0×10^{-4} mol L^{-1}. The polymer concentrations reported here are those of the polymer solution prior to mixing with the metal ion solution (the polymer concentration in the reaction medium was 1.0% lower than that before mixing). In order to examine the effect of reaction temperature on Ag nanoparticle formation, following agitation by vortex mixer for ∼10 s, the solutions were left standing in temperature range

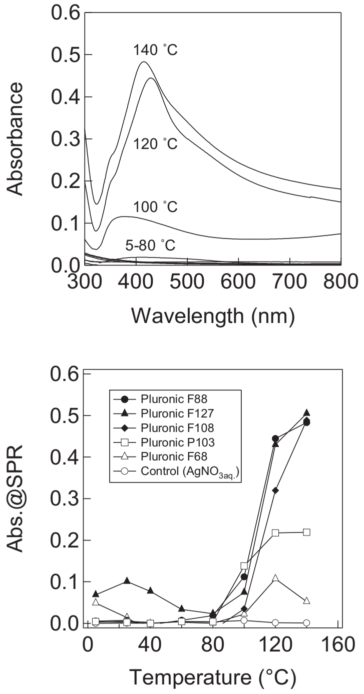

Fig. 1. (Upper panel) Absorption spectra recorded at 24 h after mixing an aqueous $AgNO_3$ solution with aqueous Pluronic F88 solution (10 wt%) at different reaction temperatures: −1, 5, 25, 40, 60 80, 100, 120 and 140 °C. (Bottom panel) Absorbance centered at ∼410 nm originating from SPR of silver nanoparticles recorded at 24 h after mixing an aqueous $AgNO_3$ solution with an aqueous PEO–PPO block copolymer solution (10 wt%): (□) Pluronic P103, (△) Pluronic F68, (●) Pluronic F88, (▲) Pluronic F127 and (♦) Pluronic F108, plotted as a function of reaction temperature. Also shown are (○) absorbances at 410 nm of aqueous $AgNO_3$ solution left standing at 5, 25, 40, 60 80, 100, 120 and 140 °C for 24 h, as control experiments.