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Manipulation of silver nanostructures using supercritical fluids in the presence of polyvinylpyrrolidone and ethylene glycol

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ABSTRACT

This study reports on a new method for manipulating the size and shape of silver nanostructures using supercritical carbon dioxide (CO_2) in the presence of polyvinyl pyrrolidone (PVP) and ethylene glycol (EG). The temperature and pressure of CO_2 as well as the ratio of the capping agent PVP to the precursor of silver nitrate are used to control the growth of the silver nuclei and grains during the synthesis of silver nanostructures in ethylene glycol. The as-synthesized nanostructures were characterized by UV–vis spectroscopy, transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), and X-ray powder diffraction (XRD). The results indicate that the aspect ratio of silver nanostructures, in particular, increases with an increase in the temperature and pressure of supercritical CO_2 from 3.5 to 50.

1. Introduction

The physical properties of metal nanomaterials are strongly dependent on the size, dispersion, and shape of their constituent particles [1,2]; hence, in order to obtain desired properties, it is important to be able to control the morphology of metal nanomaterials. Metal nanostructures attract considerable interest because of their applications in microelectronics, photonics, and optical devices [3–6]. Because the properties, and hence, the resultant applications of nanomaterials are primarily governed by their morphology and the size of their particles, it is possible to manufacture customized metal nanomaterials with unique properties. In recent years, substantial effort has been directed toward developing shape-controlled synthesis of metal nanoparticles [7–13]. Silver is an important metal that is used in traditional industries, microelectronics, electronics and photonics, medicine, and health care. The small size of silver nanostructures results in a high number of surface atoms, enhanced chemical properties and activities, a low sintering temperature, and a high electrical conductivity. Hence, there has been an increasing attention in the preparation of silver nanoparticles using supercritical fluids (SCFs) [14–17].

SCFs exhibit gas-like mass transfer properties but liquid-like solvation capabilities. Further, owing to their high diffusivity and low viscosity, they are capable of penetrating solutions and materials and accelerating reactions. The density of SCFs can be continuously altered by manipulating pressure and temperature, thereby enabling the solution strength of the SCFs to be tunable [18]. In most cases, SCFs are used to obtain particles with a narrow size distribution [19–22]. Moreover, SCFs can be used as processing media for nanostructure devices [23–25]. The increasing number of scientific and industrial research groups worldwide conducting research in SCF technology attests to its importance in the development of nanotechnology. Of the many possible SCFs, carbon dioxide (CO_2) is the one most frequently used as a solvent in material synthesis and processing. Researchers have promoted CO_2 as a sustainable and green solvent because it is inexpensive, nontoxic, nonflammable, and nonpolluting, and because it has a moderate critical temperature and pressure ($T_c = 31.1\,°C$ and $P_c = 7.38$ MPa). However, as CO_2 has zero dipole moment and a low dielectric constant, its charge-separated molecular system results in low polarity and high electrostatic interactions. Thus, most of hydrocarbon-based surfactants are not suitable in the case of CO_2 solvents [26–28]. Nevertheless, supercritical CO_2 has significant potential for applications involving CO_2-solvent-based systems that can be used for various particle synthesis processes.

In our previous study, we used SCFs with varying solvations and surfactant tails to synthesize well-dispersed silver nanoparticles [29]. These SCFs were used to manipulate the properties of the silver nanostructures and enhance the dispersive ability of the nanoparticles in liquids. Accordingly, in this research, synthesize silver nanostructures by means of a polyol process using SCFs; the polyol process was used to obtain a reactive solution that rapidly attains supersaturation in order to increase the nucleation rate of silver and

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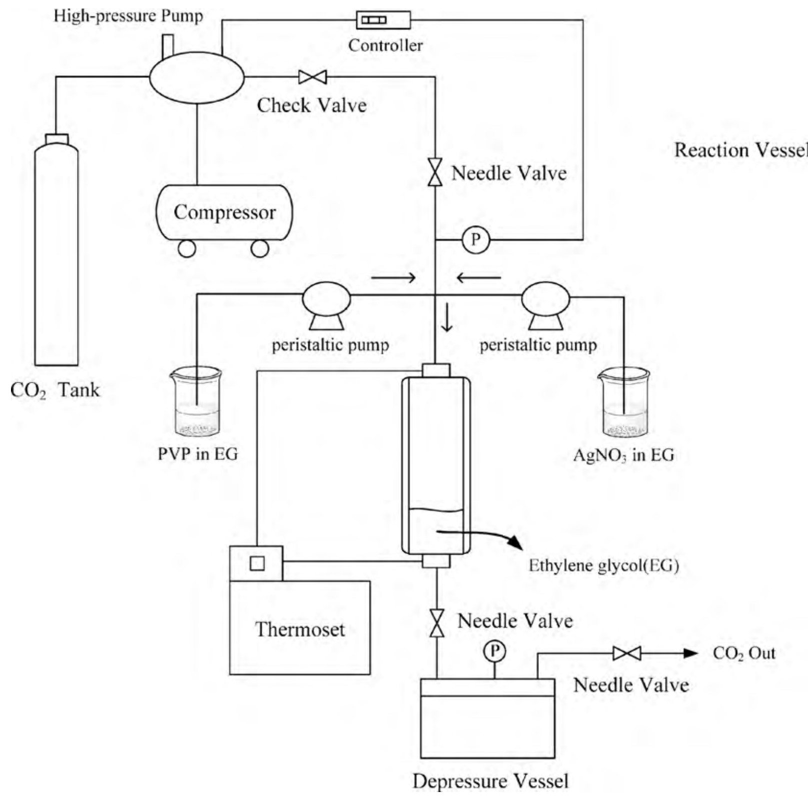

Fig. 1. Schematic diagram of supercritical CO_2 process apparatus in this study.

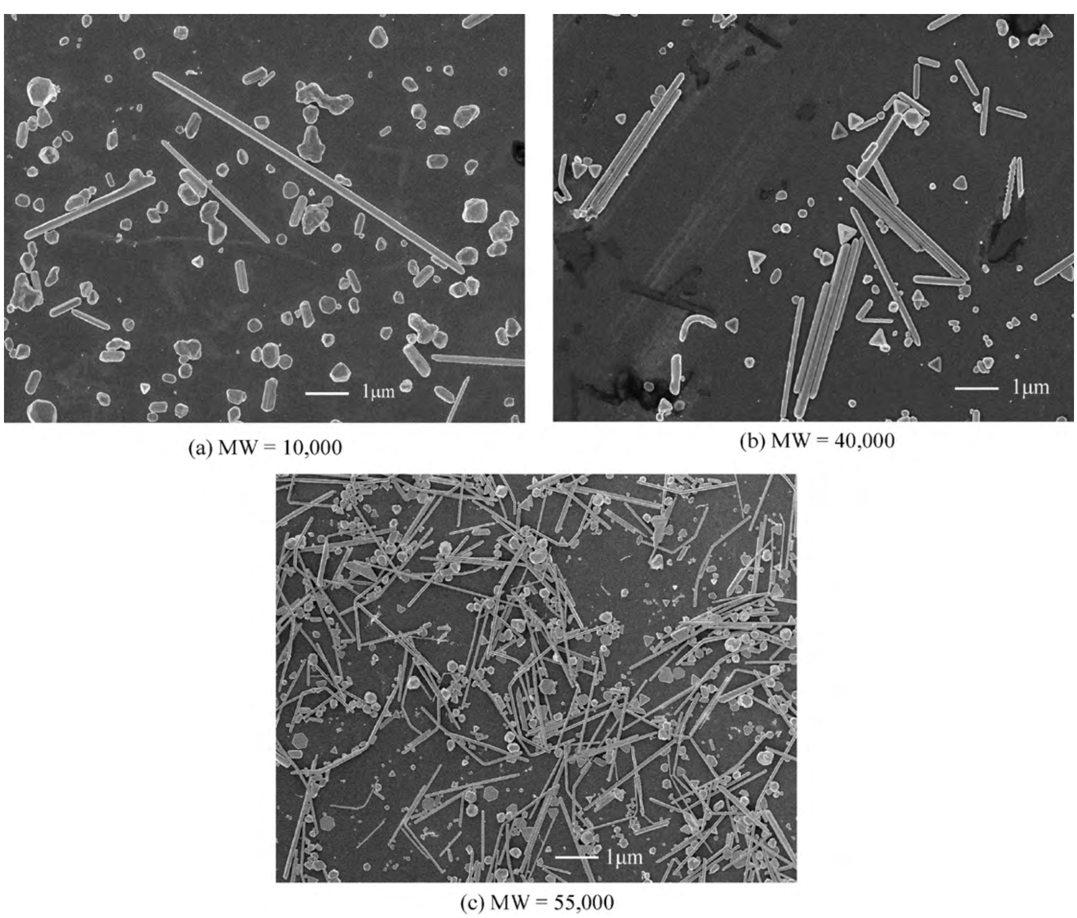

Fig. 2. FESEM images of as-synthesized Ag nanostructures at 100 °C and 25 MPa for various molecular weights of PVP in the molar ratio of $PVP/AgNO_3 = 0.003$.