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Selective adsorption of PVP on the surface of silver nanoparticles: A molecular dynamics study

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ABSTRACT

The use of surfactants to affect the shape evolution of silver nanoparticles is explored. This allows one to fine-tune the morphological evolution and the optical properties of the metal nanoparticles. Polyvinyl pyrrolidone (PVP) has been used as a surfactant to control the growth of silver nanoparticles at room temperature. In this paper, molecular dynamics simulations were performed to understand regio-selective adsorption of PVP that leads to the preferential growth of silver nanoparticles in dimethylformamide (DMF). The interaction energies between PVP and Ag(1 1 0), Ag(1 0 0) and Ag(1 1 1) crystal planes were calculated and in addition the length density profile of the surfactant on silver surfaces was also examined. Importantly, it has been demonstrated that the length distribution profiles analysis obtained from the molecular dynamics study fully explained the adsorption of PVP on the surface of silver nanoparticles through the carbonyl group of the PVP ring. The application of molecular dynamics simulation technique is important in understanding the evolution of silver nanoparticles and is vital in choosing the right surfactants.

1. Introduction

Metal nanoparticles have been the core interest of many researchers in areas of nanotechnology and nanoscience due to their interesting properties and their ease of synthesis [1–3]. The unique properties (such as optical, and electronic) of silver nanoparticles have led to extensive research focusing on these materials. These properties have been widely exploited in various applications such as photonics, electronics, optoelectronics, catalysis, information storage, photography, imaging, sensing and biological labelling [4–10]. The application of metal nanoparticles in all these aforementioned areas depends mainly on their physico-chemical properties such as composition, size, shape, crystallinity and structure. In pursuit of these applications, several approaches have been developed to produce silver nanoparticles with the required physico-chemical properties (shape and size) to fine-tune their properties toward certain applications [11–15]. The shape and size control of silver nanoparticles is of particular significance as it determines their optical properties and thus their appropriate application area. Previous studies have shown that the shape of silver nanoparticles could determine the number and position of peaks in surface plasmon resonance (SPR) measurements as well as in Surface Enhanced Raman Scattering (SERS) [16–18]. Studies have also shown that metal nanorods of particular aspect ratios lead to a significant red-shift in longitudinal SPR as a result altering the optical properties of silver nanoparticles [19].

Anisotropic silver nanoparticles such as nanoplates can be useful as effective substrates for SERS due to their red-shifted spectral absorption in the range of 700–800 nm as compared with silver nanospheres, which absorb UV–visible light in the range of 400–500 nm for particle size of less than 20 nm [8,20]. The tremendous growth for the usefulness of silver nanoparticles in many applications has led to the development of various shape-controlled synthesis approaches [21–23]. It has been shown that the effective control of the shape of silver nanoparticles is determined by factors such as precursor concentration, molar ratio of the surfactant and silver salts as well as regio-selective adsorption of surfactant on the surface of silver nanoparticles [24]. Studies have also indicated that the selective adsorption of polyvinyl pyrrolidone (PVP) could lead to different growth rates along different crystal planes; as a result the growth of silver nanoparticles yields different shapes [15]. Recently, we have published a Density Functional Theory (DFT) study to indicate the regio-selective adsorption of PVP on the surface of silver and gold nanoparticles [25]. In that study, it was demonstrated that the carbonyl end of the N-vinyl pyrrolidone (PVP monomer) is the key in the adsorption of PVP when compared to the nitrogen group of the same monomer. We also showed the kinetic evolution of silver nanoparticles with different shapes when the solution of silver nanoparticles is left undisturbed for

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