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Time dependence of nucleation and growth of silver nanoparticles

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ABSTRACT

This paper describes a simple procedure based on the modified silver-mirror process for the preparation of colloidal silver quantum dots (diameter ≤7 nm). All reactions were monitored with respect to reaction time by using UV–visible studies to understand the growth kinetics and the influence of different [ammonia], [glucose] and temperature on the formation of silver nanoparticles. Shape of the reaction–time curves (sigmoid facing up and sigmoid facing down) strongly depend on the [NH_3]. Glucose concentrations have no significant effect on the progress of the reaction. For the nucleation and growth processes, surface plasmon absorbance is directly proportional and increase–decrease with increasing [NH_3], respectively. Transmission electron microscopy (TEM) results show that the quantum dots are aggregated in an irregular manner, resulting in the formation of branches-like structures of silver. The activation energy, enthalpy and entropy of activation have been evaluated. Mechanism consistent with the observed kinetics results has been suggested.

1. Introduction

Advanced nanoparticles and/or nanoclusters of silver are one of the most commonly utilized nanomaterials due to their antimicrobial properties, high electrical conductivity, and unique optical properties because they support surface plasmons [1,2]. At specific wavelengths of light the surface plasmons are driven into resonance and the silver nanomaterials have a distinct color that is a function of their size, shape, and environment. The plasmon resonance is responsible for their yellow color in solution. Any visible change to the color of the nanoparticles in solution typically indicates that the aggregation state of the nanoparticles has changed. Great effort has been devoted to the synthesis of one- and two-dimensional (1D and 2D) monodispersed nanocrystals of silver [3–6]. Qi and Dai prepared silver nanoclusters with various morphologies ranging from the leaflike to flowerlike hierarchical structures from the silver mirror reaction (Tollen's test) by removing the copper oxide layer from commercially available copper foils under different conditions [7]. Huang and Mau have demonstrated by using silver Tollen's reaction that the carbon nanotubes prepared by the pyrolysis of iron(II) phthalocyanine can selectively grow on a SiO_2 surface when the SiO_2 wafer is patterned by silver [8]. Role of different surfactants as growth modifiers in the synthesis of silver nanoparticles and their effect on the on fundamental characteristics of silver nanoparticles prepared by modified Tollens process was studied by Soukupova and his coworkers [9]. Novel silver nanomaterials having different morphologies such as nanocubes, nanotubes, etc. structures also are produced from the silver mirror reaction [10–15].

Yu and Yam [16] developed a method to the preparation of silver nanparticles of various morphologies such as triangular particles, rods, wires and cubes, in water by *n*-hexadecyltrimethylammonium bromide modified silver mirror reaction at 120 °C. The Tollens' test is important in carbohydrate chemistry, for proof of structure. The test is specific for reducing sugars. The purpose of adding the ammonia water is to weaken the reduction of silver ion [17], which makes more beautiful silver.

$$Ag^{+} + e^{-} \rightarrow Ag^{0} \quad E_0 = 0.799 \quad V \tag{1}$$

$$Ag(NH_3)^{+} + e^{-} \rightarrow Ag^{0} + 2NH_3 \quad E_0 = 0.373 \quad V \tag{2}$$

The Eq. (2) indicates that ammonia forms a complex with silver ion, which is more difficult to reduce than silver ion itself. Addition of the first ammonia results in the exclusion of not one but two water molecules from the inner solvation shell, selectively reducing the equilibrium constant for the first association. This is not surprising because silver ion forms a more stable complex with ammonia

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