Synthesis of Silver Colloids: Experiment and Computational Model

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Abstract

We summarize our recent results [1] that model the formation of uniform spherical silver colloids prepared by mixing iso-ascorbic acid and silver-amine complex solutions in the absence of dispersants. We found that the experimental results [2] can be modeled effectively by the two-stage formation mechanism used previously to model the preparation of colloidal gold spheres [3]. The equilibrium concentration of silver atoms and the surface tension of silver precursor nanocrystals are both treated as free parameters, and the experimental reaction time scale is fit by a narrow region of this two-parameter space. The kinetic parameter required to match the final particle size is found to be very close to that used previously in modeling the formation of uniform gold particles, suggesting that similar kinetics governs the aggregation process. The model also reproduces semi-quantitatively the effects temperature and solvent viscosity on particle synthesis.

1. Introduction

Highly dispersed uniform particles are widely used presently in various areas of technology and medicine. While theoretical and computational modeling of chemical synthesis of colloids and nanoparticles has advanced recently, more progress needs to be made in understanding the complex phenomena involved, which take place over multiple length and time scales. Here we report computational modeline of the size distribution of secondary polycrystalline colloid particles produced by aggregation of primary nanosize crystalline precursors. Although initially colloidal dispersions of narrow size distribution were widely thought to consist of monocrystalline particles [4]. experimental evidence [5-8] showed that, in many cases, the final particles are in fact polycrystalline. Since aggregation of diffusing particles generally produces a widening size distribution, explanation of the narrow size distribution presented a theoretical

challenge. Several aggregation models that could produce narrow size distributions were proposed [3,9,10].

In particular, a model which yielded size distributions with narrow (relative) width by a twostage process, coupling initial nucleation of primary nanocrystals with the aggregation of these nanocrystals into secondary particles, was developed [3]. In this model, the initial fast nucleation of nanocrystals leads to a sizeable peak of small secondary aggregates. If the nucleation rate of nanocrystals then decreases in time according to a proper protocol, as occurs naturally in the nucleation process, then the initial peak of the secondary aggregate distribution grows to larger sizes, while few additional secondary aggregates are formed.

Thus a well-defined peak of secondary particles grows with its average size increasing much more rapidly than its width, resulting in a narrow size distribution. An important simplification was to approximately account for the growth of primary particles after nucleation, as well as the absorption of monomers (atoms, molecules) by the secondary particle distribution, with the assumption that the aggregating primary particles were (experimentally determined) uniform size throughout the process. In addition, from experimental observations, the secondary particles were assumed to compactify rapidly into spheres with the bulk density, on time scales much faster than that of the diffusive processes. This allowed the Smoluchowski rate [11] $K_{\bullet} = 4\pi R_{\bullet} D_{i}$ for the diffusive capture of smaller particles with diffusion constant D_1 by a larger particle with radius R_i , to be used as a basis for the aggregation rates of primary particles. The Smoluchowski rate corresponds to an assumption of a diffusion-limited process, i.e., "instantaneous" reaction/merging of the smaller particles with the larger particle.

In general, with $N_s(t)$ denoting the concentration of secondary particles containing s primary particles, the rate equations for aggregation of secondary particles can be written

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remarked you live near at hand and can catch it at its best A common belief in regard to loch fishing is that the tyro and the experienced angler have nearly the same chance in fishing the one from the stern and the other from the bow of the same boat Of all the absurd beliefs as to loch fishing this is one of the most absurd Try it Give the tyro either end of the boat he likes give him a cast of ally flies he may fancy or even a cast similar to those which a crack may be using and if he catches one for every three the other has he may consider himself very lucky Of course there are lochs where the fish are not abundant and a beginner may come across as many as an older fisher but we speak of lochs where there are fish to be caught and where each has a fair chance Again it is said that the boatman has as much to do with catching trout in a loch as the angler Well we dont deny that In an untried loch it is necessary to have the guidance of a good boatman but the same argument holds good as to stream fishing Silver Colloids Ronald J. Gibbs, 1999 The Colloidal Salts Harry Boyer Weiser.1928 The Physical Properties of Colloidal Solutions Eli Franklin Burton, 1938 The Physical Properties of Colloidal Solutions Eli Franklin Burton, 1916 Colloids Hugo Rudolph Kruyt, 1930 The Colloidal and Crystalloidal State of Matter Paul Waldemar Rohland, 1914 The Nucleation and Growth of Colloidal Silver Chloride Michael John Insley, 1963 Colloidal Silver with Lecithin, in the Treatment of Malignant Tumors George Louis Rohdenburg,1915* Therapeutical Colloids, 1913 The Elements of Colloidal Chemistry Herbert Freundlich, 1925

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