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Sodium Ascorbate Method for the Synthesis of Colloidal Palladium Particles of Different Sizes

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Multiple labeling with colloidal gold (cAu) particles of two or three different sizes has been the predominant technique during the 30 years since Frens [1] introduced the citrate reduction method, which generates monodisperse gold particles over a broad range of diameters. Recently, we have developed two new approaches to multiple labeling that utilize colloidal particles of different shapes and elemental compositions [2]. In order to maximize the versatility of this new methodology and optimize labeling efficiency, it is essential that these particles be available in a wide variety of different sizes. Unfortunately, Frens' citrate method and the subsequent tannic acid reduction technique developed by Slot and Geuze [3] have not proven effective for the synthesis of other noble metal sols in a range of particle diameters.

In order to make noble metal particles of different sizes, we had instead revisited the nuclear sol technique developed by Zsigmondy [4] nearly a century ago in which additional metal is condensed around previously synthesized nuclei a few nanometers in diameter [5]. The size of the particles is directly proportional to the concentration of the metal salt and inversely proportional to the amount of nuclei added. Although certainly of utility, especially in its capacity to prepare multimetallic particles, Zsigmondy's method is more complex than that of Frens, which combines the phenomena of particle nucleation and subsequent growth in a single procedure. Furthermore, additional refinement of Zsigmondy's sols is required in order to separate the remaining nuclei from the grown particles.

Because of these drawbacks, we have continued to pursue methodologies analogous to Frens' in which the particle size is dependent solely upon the concentration of the reducing agent. Towards this end, we have succeeded in preparing cPd particles ranging in diameter from 6.6 to 11.7nm by reduction of a palladium salt with sodium ascorbate in decreasing concentration (table 1). Although the size range of cPd particles prepared by ascorbate reduction is not nearly as broad as that of cAu particles prepared by citrate reduction, it does fill neatly the important void between the sub-5nm range prepared by reduction with molecular hydrogen or sodium borohydride and the particles greater than 18nm in diameter which can be prepared using various manifestations of the ascorbic acid reduction method [2]. The cPd particles prepared by ascorbate reduction are monodisperse, having coefficients of variance of approximately 15 to 20%, and are grown in the presence of a small amount of trisodium citrate which in this case does not reduce the metal salt, but rather stabilizes the particles against flocculation most likely through strong adsorption to the particle surface. If the particle diameter is influenced in part by the amount of citrate available for adsorption, then it might be possible to expand the size range by adjusting the citrate concentration as well. Interestingly, when the ascorbate method is applied to the reduction of platinum salts, particles of around 2.5 to 3.0nm in diameter result, regardless of ascorbate concentration.

References

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[6] The authors gratefully acknowledge support from NIH/NIGMS grant #63001.

TABLE 1. Average diameters of cPd particles prepared by reduction of 500μM K_2PdCl_4 with varying concentrations of sodium ascorbate at 100°C. Reduction occured in the presence of 0.04% trisodium citrate as a stabilizing agent.

Sol	[Na Ascorbate] (%)	Average Diameter (nm)	$\sigma_n/\bar{x}_n$ (%)
1	0.2	6.6 ± 0.07	14.7
2	0.05	7.9 ± 0.09	17.8
3	0.01	10.1 ± 0.10	15.0
4	0.005	11.7 ± 0.17	21.5

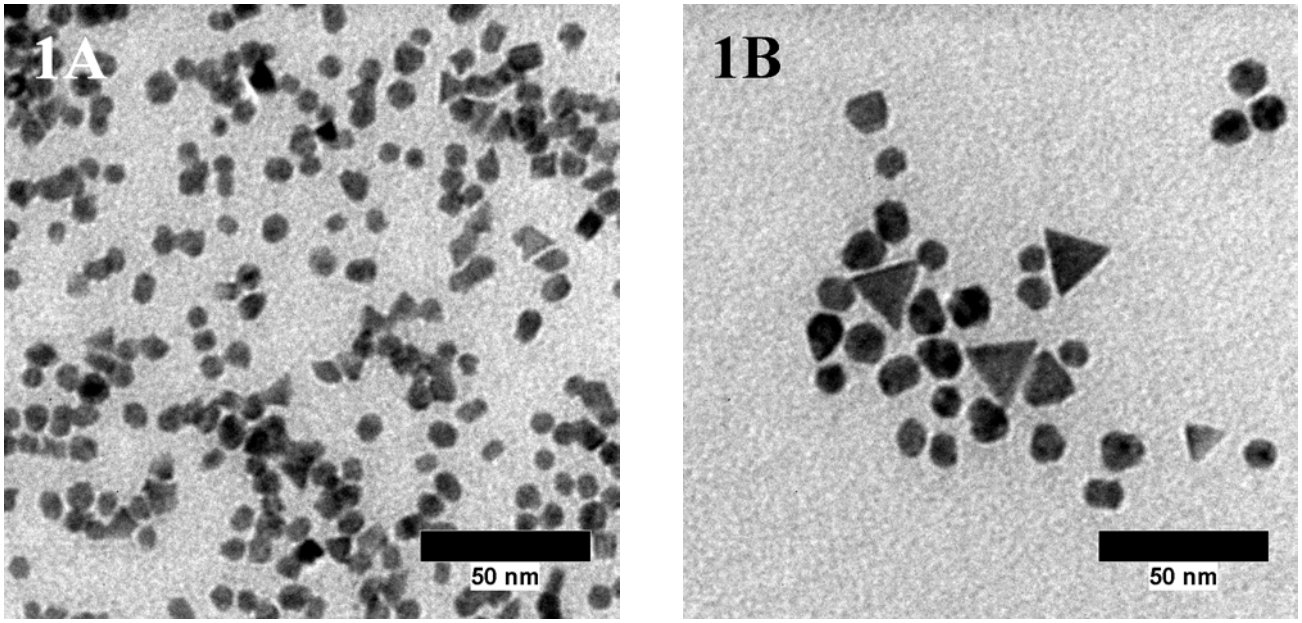

Figure 1. Transmission electron micrographs showing cPd particles prepared by reduction of 500μM K_2PdCl_4 with varying amounts of sodium ascorbate in the presence of 0.04% trisodium citrate at 100°C. Images taken at a magnification of 80,000 times and an accelerating voltage of 120KeV using a LEO 912 EFTEM. Bars are both 50nm. 1A. 6.6nm cPd particles prepared by reduction with 0.2% sodium ascorbate. 1B. 11.7nm cPd particles prepared by reduction with 0.005% sodium ascorbate.

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