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Sarah Al Gharib, Jean-Louis Marignier, Adnan Naja, Abdel Karim El Omar, Sophie Le Caër, et al.. Key Role of the Oxidized Citrate Free Radical in the Nucleation Mechanism of the Metal Nanoparticles Turkevich Synthesis. 31st Miller Conference on Radiation Chemistry, Sep 2019, West Cumbria, United Kingdom. 2019. cea-02328526

HAL Id: cea-02328526

<https://cea.hal.science/cea-02328526>

Submitted on 23 Oct 2019

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P16: Key Role of the Oxidized Citrate Free Radical in the Nucleation Mechanism of the Metal Nanoparticles Turkevich Synthesis

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The step-by-step mechanism of the citrate oxidation, of the silver ion reduction [1] [2] into atoms, and of the nucleation of nanoparticles by the Turkevich method [3] are deduced from the gamma- and pulse radiolysis yields of dicarboxy acetone (DCA), H₂ and CO₂ and of silver ion reduction. Our results demonstrate that the stronger reductant is not citrate (Cit) but the oxidized radical Cit(-H)[•]. The formation yields of DCA and CO₂ confirm the decarboxylation process during the Cit(-H)[•] oxidation. In pulse radiolysis of solutions of sodium citrate and silver perchlorate, the transient spectra [4] and the kinetics are observed from 20 ps to 800 ms. In particular, the successive H abstraction from citrate by OH[•] radicals, then the one-electron transfer from the citrate radicals Cit(-H)[•] to silver ions initiating the simultaneous nucleation and growth of the reduced silver oligomers are observed. The knowledge of the nuclearity-dependent kinetics and thermodynamics of silver atoms, oligomers and nanoparticles in solution is used to bracket the standard reduction potentials of the first ($\geq 0.4 V_{\text{NHE}}$) [2] and the second one-electron transfers from citrate ($\leq -1.2 V_{\text{NHE}}$) [2]. During the Turkevich synthesis, the Cit(-H)[•] radical was shown to be released in the bulk solution from the citrate oxidation by Ag⁺ adsorbed on the walls (Figure 1), or directly by the trivalent Au^{III} ions present in the bulk, respectively. Then the strong Cit(-H)[•] reductant alone is able, as in radiolysis, to overcome the thermodynamic barrier of the very negative potential for the reduction of the free monovalent ions into atoms that is required to initiate the nucleation and growth (Figure1). The reduction potentials values of citrate and Cit(-H)[•] also explain part of the antioxidant properties of citrate.

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