

Easy Excess to Cu⁰ Nanoparticles and Porous Copper Electrodes with High Oxidation Stability and High Conductivity

Christian Kind and Claus Feldmann

Supporting Information

Thermal decomposition of intermediate copper citrate nanoparticles

The chemical composition of the intermediate copper citrate nanoparticles was investigated by differential thermal analysis (DTA) and thermogravimetry (TG). To this concern, the intermediately formed nanomaterial was collected from the suspension right after nucleation by centrifugation. The separated nanomaterial was carefully washed by repeated redispersion in and centrifugation from ethanol. After pre-drying in air, the obtained light blue powder was dried in vacuum at ambient temperature in order to remove excess solvent residues.

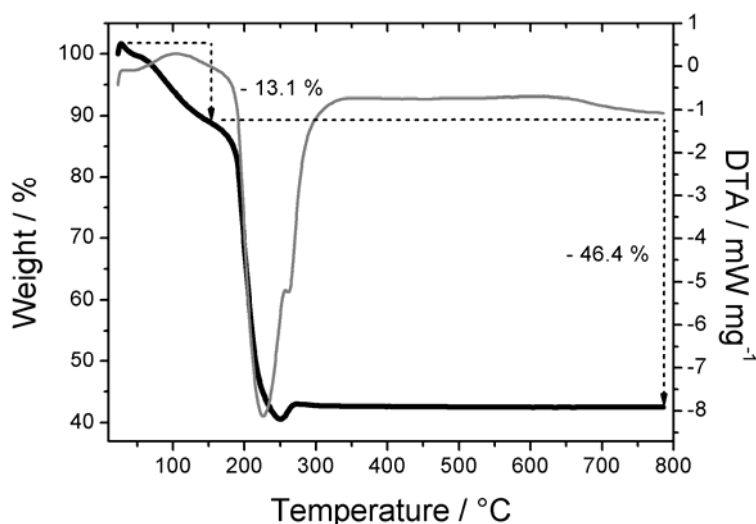
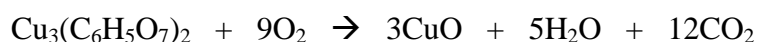


Figure S1. Differential thermal analysis (DTA, grey line) and thermogravimetry (TG, black line) of intermediate copper citrate nanoparticles as performed in air (total weight: 17.9 mg).

According to thermogravimetry, the thermal decomposition of the intermediate nanoparticles occurred in two steps (Figure S1). A first endothermic weight loss of 13.1% is

observed up to a temperature of 150 °C and followed by a second massive and exothermic weight loss of 46.4% between 150 °C and 270 °C. Thereafter, the sample weight remains almost constant. The black remnant inside of the crucible can be identified as pure CuO via X-ray powder diffraction analysis.

The observed total weight loss of about 60% is in good agreement with a composition of $\text{Cu}_3(\text{citrate})_2$ and a calculated weight loss of 58% according to the following reaction:



A stepwise decomposition is quite characteristic for bulk metal citrates (e.g. $\text{Mg}_3(\text{citrate})_2 \cdot 4\text{H}_2\text{O}$) comprising different dehydration processes at first as well as a final massive decarboxylation reaction.¹⁶ In case of the intermediate nanoparticles observed here, the second massive decomposition step at 150–270 °C represents the decarboxylation and clearly evidences the presence of molar quantities of citrate. In contrast, a composition such as $\text{Cu}(\text{OH})_2$ or CuCO_3 of the intermediate nanoparticles can be reliably excluded based on infrared spectra (cf. Figure 1) and thermogravimetry (Figure S1). Dehydration of the citrate below 150 °C is here superimposed by additional water molecules which can be either adsorbed on the particle surface or incorporated in the nanoparticles. Such adsorption/incorporation of water molecules is to be expected when considering the non-crystallinity as well as the high surface of the intermediate copper citrate nanoparticles. Taking a reproducible difference of 2–3% between the observed and the calculated weight loss into account, the composition of the intermediate nanoparticles can be conveyed in sum to $\text{Cu}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot n\text{H}_2\text{O}$ with $n = 1\text{--}3$.