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Cu Nano- / Fine-particles Covered by Polymer Nanoskin: Material for MLCC

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Abstract – Size-controlled copper nano- / fine-particles were prepared by N_2H_4-reduction of Cu_2O in the presence of soluble polymers. The obtained particles had uniform sizes and the size may be controlled by addition of ligand molecules. The obtained particles were not readily oxidized in powder form under air. The obtained particles were covered by polymer layers with the thickness of single nanometer level. These particles could be used for the *inner* electrode material of multilayered ceramics condensers, which was actually made of nickel.

Copper can be considered as a low cost and non-magnetic electro-conductive material. However, comparing with gold and silver, copper can be readily oxidized to form black CuO and brownish Cu_2O. In order to overcome this problem, doping of precious metals and wrapping with metal oxides have been considered. Doping of precious metals to copper particles may dramatically increase the cost of copper particles. In such cases, silver particles may become more cost-effective. When the particles are wrapped by metal oxides, the obtained electronic wires or electrodes always contain metal oxides which may decrease the conductivity.

We have then selected organic materials as a wrapping reagent. In most cases, wet-reduction of metal ions to obtain metal nano- / fine-particles, they are carried out in the presence of stabilizing organic compounds. Polymers, surfactants, metal-coordinative reagents have been used to control the structure, sizes, properties of metal nano- / fine-particles. Polymers have often been used to obtain metal nanoparticles applied as catalysts.[1] Polyvinylpyrrolidone and polyvinylalcohol have often been used as the stabilizing polymers. On the other hand, bio-polymers, such as gum and gelatin, were frequently used also as the stabilizing reagent of metal particles. Especially, gelatin is a cost-effective, water soluble abd metal coordinative polymer with a high gas barrier property. We, therefore, selected gelatin as a stabilizing polymer for anti-oxidized copper nano- / fine-particles.

The particles were prepared by chemical reduction of copper ions in water.[2] Hydrazine was used as the reducing reagent and used at a high pH condition. As additives, some amines or thiols can be added. Surfactants were also added in order to prevent the generation of bubbles during the reduction. The obtained dispersions of copper nano- / fine-particles were red or brown according to their sizes. The obtained nanoparticles were observed with TEM, SEM, TG-DTA, TMA analyses.

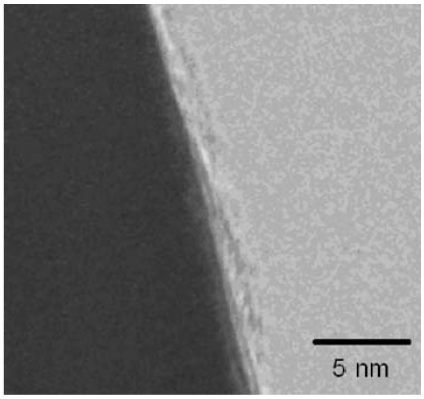

Figure 1. HR-TEM image of gelatin stabilized copepr particles.

A high resolution TEM image of the copper fine particle is shown in Figure 1. On the particle surface, one can see a gray layer on the copper particle surface. It is attributed to the organic (gelatin polymer) layers adsorbed onto the particle surface. The thickness of the gelatin layer is as small as ca. 1 nm. Thanks to this organic layer, the surface of the particles was not oxidized as also can be seen in this TEM image.

These particles were used as the materials for conductive pastes. The obtained pastes showed brownish color but after several months, some small black areas were observed in the pastes. This is probably due to the oxidization of the copper particles to CuO. The pastes were printed over BaTiO3 particle sheets to produce MLCC (multi-layered ceramics condenser) modules. Thin electrodes (thickness ~ 2 μm) could be obtained with these copper pastes. These MLCC modules worked well as a capacitor.

This study shows a possibility of the preparation of non-oxidized copper nano- / fine-particles and their capability as good materials for MLCC inner electrodes.

References

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