大気圧プラズマ電気分解による酸化銅ナノ粒子合成における pH の影響

Effect of pH on the synthesis of copper oxide nanoparticles by atmospheric-pressure plasma electrolysis

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Introduction

Recently, many researchers reported that atmospheric pressure plasma electrolysis were possible to be applied to materials synthesis such as noble metals [1] and metallic oxide materials [2-4], due to its unique ability of producing highly reactive species. Previously, copper oxide (CuO or Cu_2O) nanoparticles have been synthesized successfully by plasma electrolysis. In this work, we investigated the effect of the pH of electrolyte on the products. The results showed that Cu_2O nanoparticles couldn't be synthesized when the bulk solution was strong acidic.

Experimental Procedures

The schematic diagram of the experimental devices is shown in Fig. 1. Helium plasma in contact with electrolyte was used as the cathode, and a copper plate was used as the counter electrode. The distance between the two electrodes was 2 cm and the gap between the electrolyte surface and the tip of the tube for feeding helium was 3 mm. The electrolytes were 500 mM NaCl solutions with different pH values. The pH value of the electrolyte was measured using a pH meter. During the discharge, the current was fixed at 20 mA and the whole treatment time was 20 min.

Results and discussion

In general, the pH of solution is a nonnegligible factor in most research using an aqueous solution as well as plasma electrolysis. In our work, we adjusted the pH values of 500 mM NaCl solutions by adding different amounts of hydrochloric acid (HCl) and sodium carbonate (Na_2CO_3). The initial pH values of bulk solutions were adjusted at 10.5, 8.1, 5.0 and 2.5 by introducing the additives. After discharge, the pH values of bulk solutions were increased to 10.6, 10.1, 9.9 and 5.6, respectively.

The XRD results are shown in Fig. 2. In the cases of alkaline conditions (initial pH=10.5 and 8.1), the products were mixture of Cu_2O and $Cu_2(OH)_3Cl$. In the case of a weak acid condition (initial pH=5.0), the result was similar to the alkaline condition. However, in the case of a strong acid condition (initial pH=2.5), only the peaks of $Cu_2(OH)_3Cl$ were observed and the peaks corresponding to Cu_2O disappeared.

This result indicates that the pH value of the electrolyte has strong effect on the synthesis of copper oxide nanoparticles. Cu_2O nanoparticles cannot be synthesized in the strong acid condition. The reason is that Cu_2O is not stable in strong acid condition and it is tent to be transformed into Cu^{2+} ions by disproportionated reaction. In addition, in the case of initial pH=2.5, the bulk solution was still acidic after discharge while in other cases, the bulk solution became alkaline. This result also indicates Cu_2O nanoparticles cannot be synthesized in the strong acid condition. However, the local pH should be studied further.

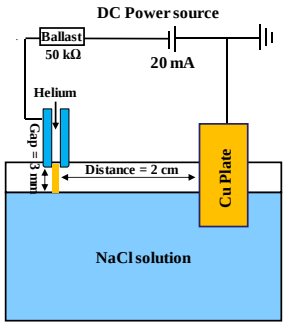

Figure 1. Schematic diagram of experimental devices

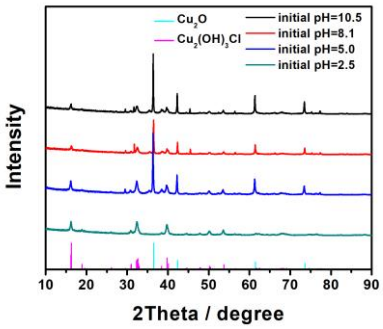

Figure 2. XRD results of products by using 500 mM NaCl solutions with different pH values as electrolyte.

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