

# Synthesis of air-stable Cu nanoparticles and their decomposition with air-exposure

T. Aoki, Y. Akiyama, M. Miyagawa, H. Tanaka

Graduate school of Science and Engineering, Chuo University, Japan

t.quya.a5v@gmail.com

Copper nanoparticles (Cu NPs) have attracted much attention because of their catalytic activity and cost-effectiveness. However, the Cu NPs generally have a problem with oxidation resistivity. In addition, hazardous reductants such as hydrazine and sodium borohydride have often been used to reduce  $\text{Cu}^{2+}$  to  $\text{Cu}^0$ . To synthesize metal NPs under mild conditions, our research group has previously developed photoreduction method [1]. Recently, we have synthesized the Cu NPs [2,3], but a long irradiation time for 24 h have been required. To solve this problem and synthesize the Cu NPs efficiently, in the present study, we have synthesized the Cu NPs with an aid of  $\text{TiO}_2$ , focusing on its high photocatalytic activity. A small amount of copper (II) acetate monohydrate ( $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ ) and  $\text{TiO}_2$  dispersion were dissolved in water containing 10 % ethanol. The mixed solution was irradiated by UV light coming from a super high-pressure Hg lamp for 5 h at room temperature. The obtained solution was characterized by X-ray diffraction (XRD) and UV-vis spectroscopy.

When the sample was irradiated by UV light for 10 min, the color at the air-liquid interface changed from light blue to reddish brown. The former and the latter correspond to  $\text{Cu}(\text{OAc})_2$  and Cu NPs, respectively. Namely, the Cu NPs were suggested to be produced from  $\text{Cu}^{2+}$  by help of the photocatalytic  $\text{TiO}_2$ . Additionally,  $\text{O}_2$  played an important role in this reduction reaction. This was also indicated by the fact that the reaction rate apparently got slowed, when the sample was degassed before UV irradiation.

The overall color of the solution turned reddish brown at 5 h of the UV irradiation. In a UV-vis spectrum of the photoirradiated solution, a strong band around 580 nm was observed due to surface plasmon resonance of the Cu NPs. In an XRD pattern of the photoirradiated sample. Both peaks at  $43.3^\circ$  and  $50.5^\circ$  assigned to  $\text{Cu}^0$  were observed, and the peaks at  $41.2^\circ$  and  $48.0^\circ$  were assigned to  $\text{TiO}_2$ . Since no peak of  $\text{Cu}_2\text{O}$  was observed at  $42.3^\circ$ , we concluded that the reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^0$  was completed, and the Cu NPs were not easily oxidized to  $\text{Cu}_2\text{O}$ , which was consistent with our previous study [4].

The produced Cu NPs were relatively stable when they were exposed to fresh air. Figure 1 shows a time evolution of the absorbance of the Cu NPs. More than 50% of Cu NPs were not decomposed even at 2 h, which were much longer than the previous study [1], where the Cu NPs protected by polyvinylpyrrolidone were totally decomposed at 20 min. In considering no use of an explicit protective agent, this high oxidation resistivity was considered to result from  $\text{TiO}_2$ .

[1] N. Nishida, Y. Kojima, H. Tanaka, Chem. Lett. 41 (2012) 926.

[2] N. Nishida, A. Miyashita, N. Hashimoto, H. Murayama, H. Tanaka, Eur. Phys. J. D 63 (2011) 307.

[3] N. Nishida, A. Miyashita, T. Tsukuda, H. Tanaka, Chem. Lett. 42 (2013) 168.

[4] H. Tanaka, T. Aoki, M. Yonemura, M. Miyagawa, K. Okumura, J. Phys. 712 (2016) 012120.

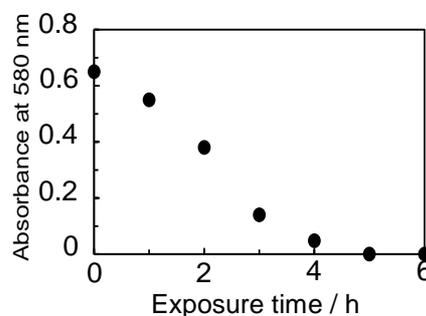


Fig. 1. Time evolution of the absorbance of the Cu NPs.