水中ラジカル反応を利用する光機能性金属ナノ酸化物作製手法の開発

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Development of Photofunctional Metal Nano Oxide Fabrication Method by Using Submerged Radical Reactions

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In this work, we developed a submerged radical reactions method for the fabrication of metal nano oxides for photofunctional applications. The radical reactions were generated by light illumination, ultrasound, and reactive oxygen species, and this method was applied for Cu, W, and Mo oxides nanoparticles fabrication. Both H_2O_2 and H_2O_2-HClO mixture solution under UV illumination could successfully generate Mo and W oxides. While for Cu oxides, HClO solution could fabricate nanorod bundles oxides. The special morphologies of the fabricated oxides indicate the potential photofunctional applications.

1. Introduction

Metal oxides are one of the most widely investigated inorganic materials because they are ubiquitous in nature and commonly used in technological applications. Recently, the wide range of nanoscale forms of these materials has gained much attention owing to their anticipated properties and application in different areas, such as photoelectron devices, sensors, catalysts, etc.

In a previous study, M. Jeem *et al.*[1] reported a new pathway for the synthesis of a variety of metal oxide nanocrystal (NC) via submerged illumination in water, called the submerged photosynthesis of crystallites (SPSC). This method is completely different from typical synthetic methods for nanoparticles, such as the hydrothermal method, solvothermal synthesis, and chemical vapor deposition (CVD). In the SPSC method, the growth of metal oxide NCs is assisted by a ‘photosynthesis’ reaction, where the metal surface is irradiated with ultraviolet (UV) light in water. Thus, the SPSC process requires only light and water and does not require the incorporation of impurity precursors. Moreover, this method is applicable at low temperature and at atmospheric pressure, producing only hydrogen gas as the by-product. These characteristics give rise to the potential application of SPSC as a green technology for metal oxide NC synthesis.

At present, flower-like NCs of zinc oxide [1, 2] and cupric oxide [3] have been successfully synthesized using the SPSC method. However, it still has two problems in SPSC process considering the further applications. First, the process is time-consuming. For example, it needs about 48 hours of UV irradiation for the fabrication of CuO by SPSC. Second, it is still difficult to apple the SPSC method to other metals, such as, W, Mo, Ti, etc., because the metal ions are difficult to generate in H_2O under light. To solve these problems, the reactive oxygen species (ROS) are introduced to the SPSC process, because it not only can improve the •OH generation by the radical reactions, which is the key process in SPSC according to our previous study[4], but also reacts with the metal substrate to generate metal ions. Therefore, the purpose of this study is to develop a photofunctional metal nano oxide fabrication method by using submerged radical reactions.

2. Experiments and results

Metal plate of Cu, W, or Mo was placed into a 20 mL cuvette with H_2O_2, HClO, and H_2O_2-HClO mixed solution, respectively. The cuvette was then irradiated by a UV lamp (UVP, B-100AP, USA, λ = 365 nm, 3.4 eV) as shown in Fig.1. The intensity of the UV irradiation was 10 – 53 mW · cm^{-2}. In some experiments, visible light (400–600 nm) and ultrasonic wave were applied in the process. After several hours UV irradiation, the obtained samples were analyzed by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM) with selected area electron diffraction (SEAD).

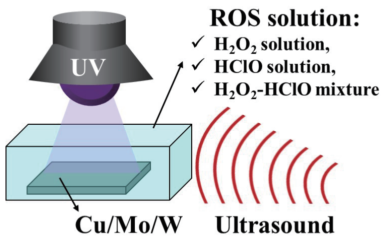

Fig. 1 Schematic diagram of the SPSC experiment

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Fig.2 shows the photos, SEM and TEM images of the powders obtained from the SPSC of W plate with H_2O_2. A yellow green powder was observed in the 10% H_2O_2 concentration of Fig.2(a-i), and a brighter yellow powder was observed in the 35% H_2O_2 concentration of Fig.2(b-i). The XRD analysis results of these materials show that the yellow-green powder is WO_3 and the yellow powder is H_2WO_4. Fig.2 (a-ii) and Fig.2 (b-ii) are TEM images of the WO_3 and H_2WO_4 powders, respectively. It was found that WO_3 and H_2WO_4 are nanoparticles with diameters of about 100 nm and 300 nm, respectively. In addition, WO_3 was found to be less crystalline and to have a flake shape, while H_2WO_4 was found to have a square plate shape. A similar study was carried with intermediate H_2O_2 concentrations in the range of 10% – 35%. As a result, it was found that WO_3 tended to form at low concentrations of H_2O_2, while H_2WO_4 tended to form at high concentrations. Both WO_3 and H_2WO_4 nanoparticles could be made easily and selectively by SPSC method.[5]

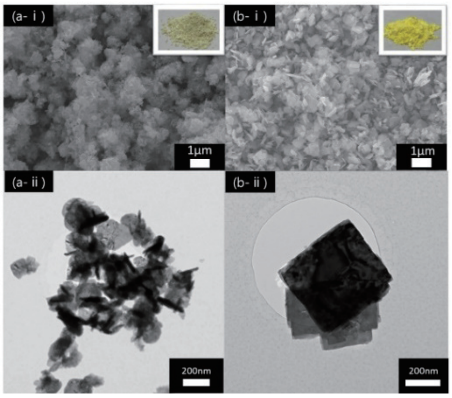

Fig. 2 (a) WO_3 (b) H_2WO_4 nano-oxides prepared using SPSC with H_2O_2: (i) SEM images, (ii) TEM images.

The reactions during this process are considered as followings:

(1) W is dissolved into H_2O_2

$$\mathrm{W + 3H_2O_2 \rightarrow WO_4^{2-} + 2H^+ + 2H_2O}$$

(2) Radical generation caused by UV irradiation

$$\mathrm{H_2O_2} + h\nu \rightarrow 2\cdot\mathrm{OH}$$

(3) WO_3 and H_2WO_4 formation

$$\mathrm{2WO_4^{2-} + 4\cdot OH \rightarrow 2WO_3 + O_2 + 4OH^-}$$

$$\mathrm{WO_4^{2-} + 6\cdot OH \rightarrow H_2WO_4 + 1.5O_2 + H_2O + 2OH^-}$$

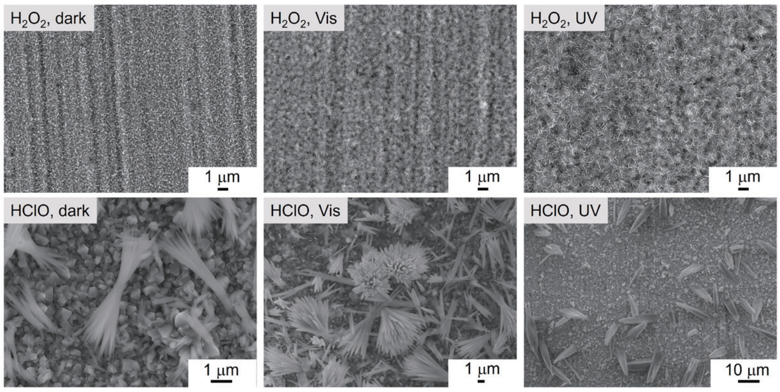

Fig. 3 SEM images of Cu plate surface after reacted with H_2O_2 (15%) and HClO (200 ppm) under different conditions (dark, visible light, UV).

We also using H_2O_2 and H_2O_2-HClO mixture solution for Mo oxides fabrication and successfully obtained nanorod α-$MoO_3 \cdot H_2O$. Interestingly, as shown in Fig. 3, when using the H_2O_2 on Cu plate, nanoparticles were not observed under dark or illumination conditions. While using HClO, the bouquet-like nanorods were obtained, which is analyzed as $Cu_2Cl(OH)_3$. The special morphologies of these metal oxides obtained by SPSC shows the potential in photofunctional application, which will be studied in the future.

3. Conclusion

ROS of H_2O_2, HClO and ultrasound wave are applied in SPSC process to improve the radical reactions for the fabrication of Cu, W, and Mo oxides, and the mechanism of the reactions are analyzed. Both H_2O_2 and H_2O_2-HClO mixture solution could successfully generate Mo and W oxides. For Cu, HClO solution could fabricate nanorod bundles oxides. The special morphologies of the obtained metal oxides are expected to photofunctional application, which will be studied in the future.

4. Acknowledgement

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