平成 28 年度　エネルギー・マテリアル融合領域研究センター　若手研究員等研究助成　報告書

研究テーマ名：Study on the mechanism of photochemical reaction during submerged photo-synthesis of crystallites ZnO	研究室名：光・熱エネルギー変換材料 氏名：張　麗華

1.研究成果の概要

1.1 Background

Based on our early research work, a new pathway of producing variety of metal oxides nanocrystallites was reported, which we call it SPSC (Submerged Photo-Synthesis of Crystallites) method[1]. In SPSC method, the initial metal surface treatment was conducted based on the utilization of the submerged liquid plasma process. After that, the nanocrystallites growth was then completed by a 'photosynthesis' reaction, where the irradiation of UV light on the nanobumps inside pure water assisted the growth of metal oxide nanocrystallites (NCs). In order to understand the mechanism of photochemical reactions during SPSC, this research work studied the pH and temperature change of the water and the morpholrgies change of the ZnO NCs during SPSC UV irradiation. Consequently, the mechanism of SPSC were propesed.

1.2 Methods

SPSC method include two steps. The first one is the plasma treatment of Zn plate. After that, in the second step, the pre-treated plate was put into ultrapure water and irradiated by UV light in a light proof chamber. During the UV irradiation, the pH and temperature of the water was monitored by a pH meter and the morphologies of the surface was observed by SEM. The weight of the Zn plate was measured by a Micro Balance. The samples were pick out from the water for the weight measurement after a certain period of UV irradiation time. A conventional-TEM was used to obtain TEM micrograph and selected area electron diffraction (SAED) pattern of the nanorods.

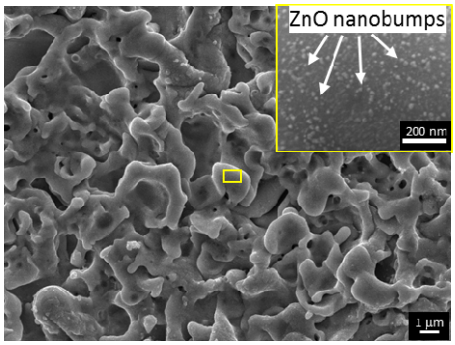

Figure 1 SEM images of Zn plate surface after plasma treatment.

1.3 Results

Figure 1 shows the SEM images of Zn plate after plasma treatment. As shown in the figure, the plasma treated plate has a protruding characteristic and many nanobumps distributed on the surface. The Nanobumps act as the seeds of ZnO NCs, and the size of nanobumps are about 10 - 20 nm.

Figure 2(a) shows the pH and temperature change during 24 h UV irradiation[2]. The water temperature was increased to about 40℃ by light energy. The pH has a sharp peak at the initial 2 hours, after that the pH changed in the range of 7.0-7.6. Figure 2(b) shows the morphologies of ZnO NCs during different UV irradiation time[2]. With 12 h UV irradiation, the nanobumps grow into nanorods (NRs). With irradiation time increasing, the length of nanorods increased and flower-like nanorods were observed by 24 h UV irradiation.

The weight measurement results showed that weight of the samples increased with UV irradiation time during the first 60-96 h. Afte that, the weight decreased. During the weight increase stage, the reaction of NCs growth is dominate. After long time UV irradiation, a lot of broken NCs were distributed on the sample surface and flower-like ZnO NCs was not observed. Therefore, the exfoliation of NCs from the substrate Zn plate was the main reason of weight decrease.

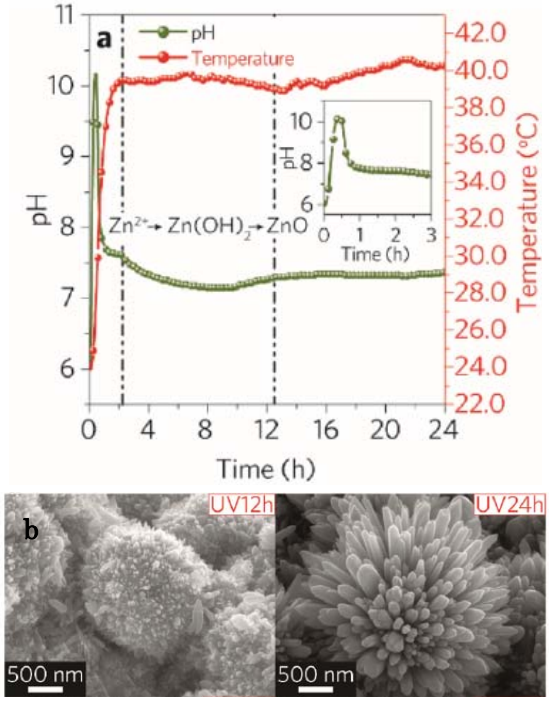

Figure 2 (a) The pH and temperature change during 24 h UV irradiation. (b) SEM images of ZnO NCs.[2]

Figure 3 shows the TEM micrograph of ZnO NRs. The right panel is its selected-area electron diffraction (SAED) pattern obtained along the $[1\bar{1}0]$ direction, and the growth direction is along the c-axis with a $(00\bar{1})$ O-terminated polar surface.[2]

Figure 3 TEM images of ZnO NR. The right panel is its SAED pattern.[2]

The photochemical reactions during SPSC were analyzed and the reactions during SPSC were considered. Both photochemical and hydrothermal reactions contribute to the SPSC. Firstly, photochemical reaction through water splitting builds holes at the bottom and electrons at the apical portion of the nanobumps. The OH radicals transform into OH^- and then reacted with Zn^{2+} to generate $Zn(OH)_2$. The decomposition of $Zn(OH)_2$ forms ZnO NRs. The net reaction could be write as following:

$$Zn + H_2O + h\nu \rightarrow ZnO + H_2$$

1.4 Summary

This work studied the morphologies change of ZnO NRs and the pH and temperature change of the water during UV irradiation of SPSC process. The results showed that OH radical, which was generated by photochemical reactions, plays an important role for the apical growth of ZnO NRs. Based on the results, the mechanisum of the SPSC was considered, in which both photochemical and hydrothermal reactions contribute to the SPSC.

Reference:

[1] Melbert Jeem, Muhammad Rafiq Mirza bin Julaihi, Junya Ishioka, Shigeo Yatsu, Kazumasa Okamoto, Tamaki Shibayama, Tomio Iwasaki, Takahiko Kato, and Seiichi Watanabe. *Sci. Rep.* 5. Article number: 11429

[2] Melbert Jeem, Lihua Zhang, Junya Ishioka, Tamaki Shibayama, Tomio Iwasaki, Takahiko Kato, and Seiichi Watanabe. *Nano Lett.*, **2017**, *17* (3), pp 2088-2093

2.研究成果発表リスト (口頭発表・論文等)

国内会議：

(1) 西野史香、Melbert Jeem、張麗華、岡本一将、渡辺精一「水中結晶光合成法による酸化銅ナノ表面構造体の創製」表面技術協会第 134 回講演大会 2016 年 9 月

(2) 高井大，西野史香，Melbert Jeem、張麗華、沖中憲之，渡辺精一，岡本一将．日本金属学会 2016 年秋期講演大会，2016 年 9 月

(3) L. Zhang, N. Okinaka, S. Watanabe. 5th Hokkaido University-Seoul National University Joint Symposium, November 25, 2016.

学術論文：

(1) Melbert Jeem, Lihua Zhang, Junya Ishioka, Tamaki Shibayama, Tomio Iwasaki, Takahiko Kato, and Seiichi Watanabe. Tuning optoelectrical properties of ZnO nanorods with excitonic defects via submerged illumination. *Nano Lett.*, **2017**, *17* (3), pp 2088-2093

(2) Fumika Nishino, Melbert Jeem, Lihua Zhang, Kazumasa Okamoto, Satoshi Okabe, Seiichi Watanabe. Sci. Rep. doi:10.1038/s41598-017-01194-5

3.研究結果のプロジェクト研究等への活用・展開予定

The SPSC method is a green technology for the fabrication of metal oxide nanostructure. Nanoparticles of ZnO, CuO, and iron oxide has been successfully obtained by SPSC. In future work, we will attempt to fabricate more kinds of metal oxides by SPSC and the further application of the obtained nanostructure will be studied.

4.特記事項

注：全体で 2 ページ以内であれば枠の大きさを自由に変更可。