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科学研究費助成事業　　研究成果報告書

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研究課題名（和文）水中結晶光合成による金属酸化物ナノロッドの創製とメカニズム解明

研究課題名（英文）Mechanism study of metallic oxide nanorods fabricated by submerged photosynthesis of crystallites

研究代表者

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交付決定額（研究期間全体）：（直接経費）　　2,500,000円

研究成果の概要（和文）：光照射を利用したナノ結晶合成の一種として、水中結晶光合成法(SPSC)を開発した。さらに、ガルバニク効果を施したSPSC処理により、異種金属ZnO/CuOヘテロナノロッドの合成に成功した。成長メカニズムを詳細に調べるには、ZnO/CuO接合界面におけるSTEM-VEELS測定、接合界面の結晶モデルに基づく電子状態の計算と光応答の測定を行った。TEM観察より、ZnO/CuOが{110}面に沿って結合し、格子の不整合性が0.5%以下であることがわかった。また、電子状態計算がCuO→ZnOの電子移動を示し、格子間亜鉛と酸素欠損の相互作用により形成された接合特有の発光に起因したことが明らかになった。

研究成果の学術的意義や社会的意義
SPSC法は、様々な金属基板に多種多様な金属酸化物のナノロッドを安価で簡便に大面積成長させることができることから産業応用上有利であり、さらに金属-金属酸化物ナノロッドの接合界面を舞台とした光エレクトロニクスや光エネルギー変換工学の学術領域の発展に貢献し、太陽電池、殺菌デバイス、ガスセンサー、光メッキ等、様々なデバイス開発にも利用できる。さらに、光と水を用いて水素と金属酸化物のみを生成する、グリーンテクノロジーであることも大きな強みである。

研究成果の概要（英文）：The research utilizes submerged photosysnthesis of crystallites (SPSC) method for metallic oxide nanostructures fabrication. Further, galvanic reaction was incorporated for facile ZnO/CuO hetero-nanorods synthesis. To elucidate the growth mechanism, STEM-VEELS, electron density of states (DOS) calculation based on crystal model, as well as optical reponse measurement were performed on the ZnO/CuO junction. On the basis of TEM observation, ZnO/CuO junction was established on {110} plane with <0.5% lattice mismatch. DOS calculation showed electrons transfer from CuO to ZnO, and interaction between interstitial Zn (IZn) and oxygen vacancy (Vo) is the reason for ZnO/CuO inheritance optical response.

研究分野：ナノ材料科学

キーワード：ナノロッド　電子顕微鏡　第一原理計算　光合成

１．研究開始当初の背景

The research focused on fabrication of metallic oxide nanostructures via submerged photosynthesis of crystallites (SPSC) method. SPSC utilizes UV to visible light illumination towards uneven metallic surface (nanobump) in water. It was proven that under ambient environment, SPSC can fabricate large scale surface of nanorods with H_2 gas production via photo-induced water splitting, which can be advantageous for real industry applications. The photo-induced water splitting occurs on the tip of nanobump, caused by oxygen vacancies (Fig. 1) (M. Jeem et al., *Nano Lett.* **17**, 2088-2093 (2017)). For ZnO nanorods case, this resulted a unique ZnO apical growth at the local cathodic, while $Zn \rightarrow Zn^{2+} + 2e^-$ reaction occurs at the local anodic.

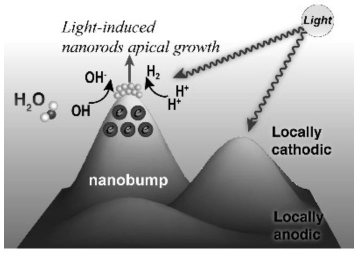

Fig. 1. Photo-induced water splitting in SPSC.

Further, a galvanic reaction can be combined to fabricate hetero-nanostructures of ZnO-M (M: Cu, Au, Pt, Ag, W, Ni) (K. Hiraiwa et al., *App. Sur. Sci.* **489**, 269-277 (2019)). A general SPSC growth reaction is given by $mM + nH_2O + hv \rightarrow M_mO_n + nH_2$ (g), which explains light absorption (hv) of metal M for metallic oxide M_mO_n growth. However, although a similar nanorods morphology observed, a unified growth mechanism of those hetero-nanostructures under galvanic combined SPSC was not clearly understood.

２．研究の目的

The research objective is to elucidate a growth mechanism for various metallic oxide nano-heterostructure under SPSC.

３．研究の方法

Metallic surface (Cu, Au, Pt, Ag, W, Ni) was first annealed or sputtered with oxide film to enable ZnO growth. For example, Cu mesh was annealed from 400 – 500 °C to get dense CuO nanowires surface. Then, the CuO nanowires mesh and Zn foil were attached by spot welding to make a galvanic contact. For SPSC treatment, the sample was immersed in distilled water and UV-irradiated for 24~72 hours to obtain ZnO/CuO hetero-nanostructure. ZnO nanorods were successfully grown on the CuO nanowires to exhibit a nanoforest morphology. Surface characterization and crystal analyses were performed with electron microscopy (FE-SEM and S/TEM) and X-ray diffraction (XRD). In particular, high-resolution TEM (HRTEM) observation, valence electron energy-loss spectroscopy in STEM (STEM-VEELS), and ab-initio calculation were performed on the boundary region of ZnO/CuO to obtain crystal defects information and their electrons density of states. Physical properties were analyzed via photoluminescence (PL) and cathodoluminescence (CL) measurements, as well as photoelectrochemical response.

４．研究成果

As shown through HRTEM observation, ZnO(001) and CuO (001) established the ZnO/CuO junction, with a mixed impurity of $ZnCuO_2$ compound (Fig. 2a). In particular, a ZnO(110) surface is more predominant throughout the surface of a ZnO nanorod grown on a CuO surface. While energy relaxation for the interface occurrence could driven the ZnO(110) surface, light irradiation effect is not trivial for the formation, as previous research have found that a local-oxygen deficient will enhance a photo-induced ZnO nanorods growth(M. Jeem et al., *Nano Lett.* **17**, 2088-2093 (2017)). On a side note, a ~0.15 Å shrinkage of ZnO(001) and CuO(001) region occurred at the interface (Fig. 2b), plausibly due to Jahn-Teller effect where electrons transfer affected the atomic coordination. Based on UV-Vis absorption spectra, the ZnO/CuO heterostructure will exhibit a peculiar absorption at ~530 nm region. Reported articles reasoned antisite defects, vacancies, band bending that resulted this absorption behavior. However, there is no solid discussion in case of using the optimized interface geometry that manifest this absorption property. This has been elucidated through STEM-EELS measurement on the ZnO/CuO interface and its DFT calculation.

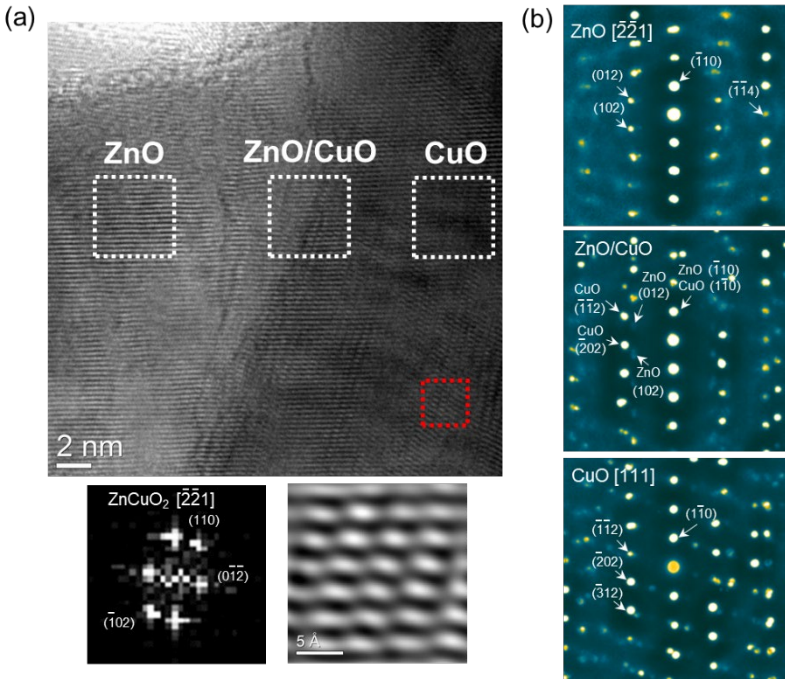

Fig. 2 (a) HRTEM image of ZnO/CuO heterostructure with marked ZnO, ZnO/CuO, and CuO region. Bottom images are ZnCuO2 FFT pattern obtained from red marked area and its FFT image, respectively. (b) TEM 1nm beam diffraction patterns respective to the ZnO, ZnO/CuO, and CuO lattice in (a).

In reference to TEM data, a ZnO(001) and CuO(001) surface were cleaved to create the ZnO/CuO interface, having equivalent ZnO/CuO mass of Zn:Cu:O to 12:12:24. The geometry was optimized through a vacuum slab (Fig. 3a). The relaxed geometry is in agreement with the plane distances in Fig. 2b, where ZnO (001) could be stretched toward shared oxygen with CuO. This behavior can be qualitatively observed through the electron transfer (Fig. 3a bottom), where electron density affinity is more pronounced in ZnO. Achieving this interface, an interband energy at 0.5 eV and 2.0 eV were established, due to electrons occupancy in Zn 3*p* and Cu 3*p*, respectively. The $ZnCuO_2$ bulk composition was determined by referring to the chemical map at the interface, where Zn is rich and deficient with copper and oxygen. Clearly, there is no interband energy in the $ZnCuO_2$ bulk but both interface and $ZnCuO_2$ shared ZnO bandgap energy of 3.3 eV. It is difficult to discuss the dielectric function peaks behavior, but using the dielectric functions, optical absorption can be interpreted in parallel with STEM-VEELS measurement (Fig. 4).

The dielectric function behavior of ZnO/CuO interface can be verified through mixing of calculated ZnO/CuO and $ZnCuO_2$. This collective electron propagation and absorption affected the interface absorption and formation. Firstly, electron transfer of Cu 3*d* and O 2*p* from the valence band occurred both in interface and $ZnCuO_2$. The interface is predominant for the 2.0 eV absorption peak, while both can lead the absorption at 3.5 eV. In view of 2.0 eV through the band bending of ZnO/CuO, this is the energy required to electrons in CuO and give rise to hole formation in ZnO to create a quasi point-defect in the interface dimension. The Cu 3*p* held responsible for the electron departure from CuO to ZnO, creating electrons occupancy at 0.5 eV of Zn 3*p*, and thus establish a hole formation in ZnO band. The electron transfer efficiency could be damped by vacancies in CuO, as well as non-stoichiometric $ZnCuO_2$. However, non-stoichiometric $ZnCuO_2$ does not play a key role to determine the peak shift of the interface absorption. Presumably, due to the dimensionality occupied by efficient electrons transfer at the interface, along with the vacancies, resulted the continuous mixing of ZnO and CuO until 40 nm at the ZnO/CuO region.

This research essentially has provided an in-depth discussion for ZnO/CuO opto-functional enhancement, opening a perspective in advancing nano-heterostructure and interface design. Furthermore, the combination of known hydrothermal method with light-induced synthesis also has patched a meaningful gateway to producing materials and devices with novel opto-functional properties.

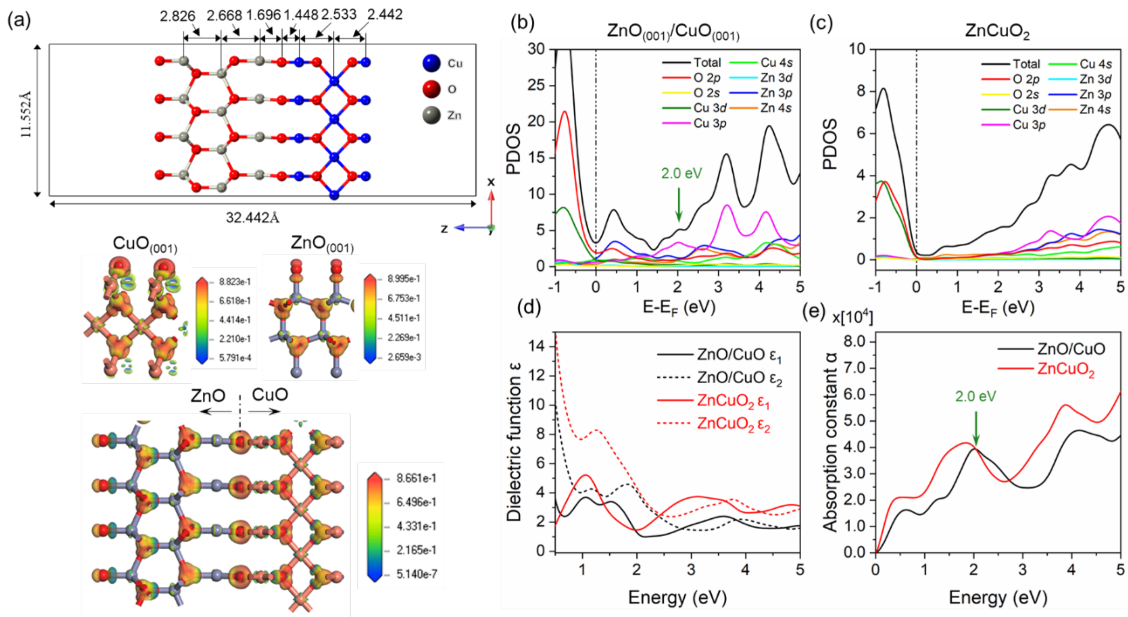

Fig. 3 (a) Optimized ZnO(001)/CuO(001) interface structure. Bottom images are electron density difference mapping for CuO(001), ZnO(001), and their hetero-interface, respectively. (b) PDOS for ZnO(001)/CuO(001) interface and bulk $ZnCuO_2$, respectively. (d-e) Calculated dielectric function (ε) and absorption coefficient (α) for both structures, respectively.

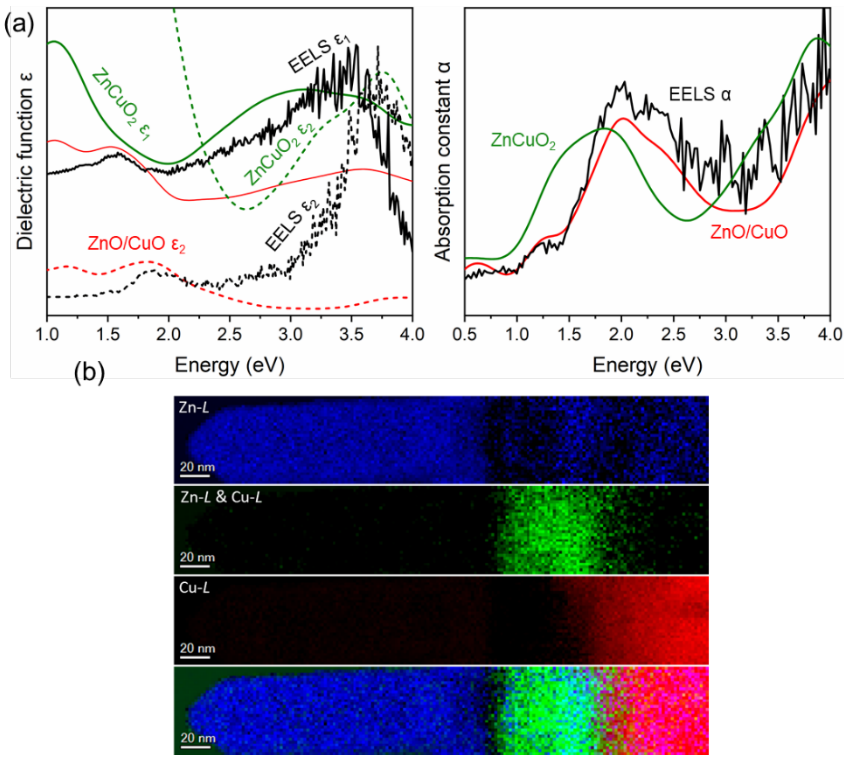

Fig. 4 (a-b) Comparison between calculated and experimental complex ε and absorption constant (α). Red and green lines are calculated ZnO(001)/CuO(001) interface and $ZnCuO_2$, while black lines are spectra from STEM-VEELS results. (b) STEM-EELS mapping on a single ZnO nanorod grown on the CuO surface.

５．主な発表論文等

〔雑誌論文〕　計3件（うち査読付論文　0件／うち国際共著　0件／うちオープンアクセス　0件）

１．著者名 Tsukamura Jumpei、Takahashi Yuki、Zhang Lihua、Jeem Melbert、Okamoto Kazumasa、Watanabe Seiichi	４．巻 256
２．論文標題 Fabrication of color-toned micro/nanopattern surface by submerged photosynthesis method	５．発行年 2022年
３．雑誌名 Microelectronic Engineering	６．最初と最後の頁 111727～111727
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.mee.2022.111727	査読の有無 無
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

１．著者名 Takahashi Yuki、Jeem Melbert、Zhang Lihua、Watanabe Seiichi	４．巻 26
２．論文標題 The origin of opto-functional enhancement in ZnO/CuO nanoforest structure fabricated by submerged photosynthesis	５．発行年 2022年
３．雑誌名 Applied Materials Today	６．最初と最後の頁 101359～101359
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.apmt.2021.101359	査読の有無 無
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

１．著者名 Murakami Shuntaro、Zhang Lihua、Jeem Melbert、Okamoto Kazumasa、Nakagawa Yuki、Shibayama Tamaki、Ohnuma Masato、Watanabe Seiichi	４．巻 124
２．論文標題 Photo- & radio-chromic iron-doped tungstic acids fabricated via submerged photosynthesis	５．発行年 2022年
３．雑誌名 Optical Materials	６．最初と最後の頁 111966～111966
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.optmat.2021.111966	査読の有無 無
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〔学会発表〕　計2件（うち招待講演　1件／うち国際学会　0件）

１．発表者名 Melbert Jeem
２．発表標題 Local oxygen-deficiency in ZnO nanorods and their opto-electrical properties measurement via STEM-VEELS
３．学会等名 微細構造解析プラットフォームワークショップ2020（招待講演）
４．発表年 2020年

１．発表者名 Melbert Jeem
２．発表標題 Low-temperature cathodoluminescence study of patterned ZnO nanorods fabricated by submerged photo-synthesis
３．学会等名 公益社団法人日本顕微鏡学会第63回シンポジウム
４．発表年 2020年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関