# 水中結晶光合成による ZnO ナノロッドの作製と光・電子特性の評価

# ZnO Nanorods Fabrication via Submerged Illumination and its optoelectrical properties

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ZnO is an attractive compound for optoelectronic devices application due to its wide direct bandgap (3.37 eV) and a large exciton binding energy of 60 meV. Under ultraviolet light excitation, ZnO can exhibit broad spectrum of visible light illumination. And by modifying its morphology, the intrinsic crystal defects will shift the visible light peak. In this study, a facile method using UV (λ = 365 nm) illumination in pure water has been employed to tune ZnO nanorods (NRs) morphology. The tunability is demonstrated by extending UV illumination time to obtain pencil-like and flat-tip shape of ZnO NRs. [1,2]

On the basis of STEM-EDS mapping result, it is known that oxygen vacancy ($V_O$) exists on a pencil-like NR. The $V_O$ content decreased during NRs transformation to flat-tip shape. During this phenomena, blue shift (605-523 nm) in photoluminescence (PL) spectra was observed. Here, PL results apprised of the $V_O$ existence because of its high energy resolution (<1 meV). However, PL method is lack of spatial resolution to study the $V_O$ point defect on a NR.

On the contrary, STEM-valence electron energy loss spectroscopy (VEELS) has sub-angstrom spatial resolution advantage. Thus, STEM-VEELS measurement was conducted on a pencil-like NR. By using the VEEL spectra, dielectric function was derived through Kramers-Kronig analysis. Comparing with the bulk part, a double increase of Im(ε) in complex dielectric function (ε = Re(ε) + Im(ε)) on near band edge of ZnO (3.3 eV) was observed on the tip-edge of pencil-like NR (Fig. 1). This translates to greatest energy loss arise at the tip-edge and explains the NRs apical growth behavior.

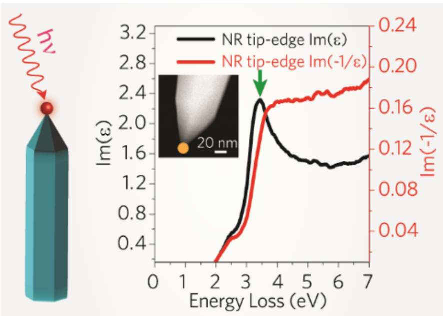


**Fig 1. Left**- Optoelectrical hotspot during light interaction on tip-edge of a NR. **Right**- Im(ε) peak at 3.3 eV of the NR.

An ab-initio calculation also was performed to confirm the Im(ε) and other optoelectrical results. The ab-initio calculation was in good agreement with the experimental VEELS, as well as confirming the unchanged bandgap value during tapered-capped NR transformation.

The PL, STEM-VEELS and ab-initio results highlighted the $V_O$ point defects in a tapered NR serve as an optoelectrical hotspot for the NR light-driven formation. STEM-VEELS technique indeed has opened assortment of outlook in this study, especially to studying nanostructures optoelectrical properties. The demonstration of this technique can be extended to study such growth behavior for other metal oxide systems.

**References** [1] M. Jeem, *Sci. Rep.* **5**, 11429 (**2015**). [2] M. Jeem, *Nano Lett.* **17**, 2088-2093 (**2017**).