学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Submerged photo-synthesis of ZnO nanorods and their opto-electrical properties
(ZnO ナノロッドの水中結晶光合成と光・電子特性)

Semiconductor nanomaterials have long been designed for application in opto-electronic devices, photocatalytic materials, biological materials and several more. This is because when the size of semiconductor materials is reduced to nanoscale, their physical and chemical properties drastically change. The result is novel and unique properties suitable for those type of applications. Besides TiO_2, ZnO has been of interest over the past two decades, because of its wide bandgap energy of 3.37 eV and high exciton binding energy of 60 meV. While many effort has been spent to study ZnO nanomaterials, there is still lack of understanding its formation mechanism. Recently, a facile method to synthesis ZnO nanocrystallites using submerged liquid plasma has been introduced to fabricate crystal seeds on a metallic Zn surface. Further, a UV (λ = 365 nm) light irradiation on the crystal seeds in ultrapure water addresses a new green technology method for this type of nanocrystallites fabrication. The thesis focused on expanding this framework to many types of metals and control their nanocrystallites morphology. The common characteristic shared by all implemented materials is their sharp apical growth morphology, which is driven by light irradiation effect. Studying this effect through crystal defect change in ZnO nanorods have given a perspective for its application in opto-electronic devices. Finally, the work is expanded to a new field: patterning and antimicrobial effects study using the same method.

Chapter 1 gives a brief introduction of TiO_2 and ZnO in their 1-D to 3-D nanomaterials processing. Here, the fundamental of this thesis is established. The potential of ZnO nanocrystallites in opto-electronic devices application is discussed. Conventional formation mechanism regards crystals defect in alkaline solution influencing the morphology change of ZnO nanocrystallites. The issue is no framework have been dedicated to study local crystal defects occurred by light irradiation in pure, neutral water. Thus, the objective of the thesis is to implement light irradiation effect to ZnO nanocrystallites formation and study their opto-electrical properties.

Chapter 2 introduces submerged liquid plasma as a facile method to fabricate crystal seeds (nanobumps), which are the localized oxide nanoparticles on a metal plate surface. The target material is set as cathode, while a platinum wire bended into mesh is set as anode. There are two types of plasma discharge: glow-discharge and arc-discharge. The initiation control of both is essential in order to get the nanobumps surface and preventing the electrode from getting burned. A typical voltage and current ranges during glow-discharge on a Zn plate is 130 – 140 V and 1.9 – 2.0 A, respectively. Nanobumps are the nanosized metal oxide (ZnO) particles. Their transformation in construction of nanocrystallites later instate the advantage of their modified band energy structure. This is highlighted in photochemical reactions when an ultraviolet (UV, λ = 365 nm) irradiation on the nanobumps was implemented.

Chapter 3 introduces the production of ZnO nanorods forming into nanoflowers and dendrites by using submerged photosynthesis of crystallites (SPSC) technique. Other than ZnO, SPSC technique also can be utilized to fabricate CuO nanoflowers, CeO_2 dendrites, and WO_3 nanorods. In particular, the ZnO nanorods are shown to grow at the protruded surfaces (nanobumps) when illuminated by ultraviolet (UV, λ = 365 nm) in pure, neutral water. The process is photocatalytic, with hydroxyl radical via water splitting and hydrogen gas were detected. Ab initio calculation was conducted to verify high electron density at nanobumps surfaces. This is essential to enable water splitting occurrence at low dissociation energy.

Chapter 4 highlights the apical characteristic control on ZnO nanorods, which evolves from tapered to capped shape after continuous 72h UV irradiation. Then, the capped shape will reconstruct again into tapered shape after UV re-irradiation in fresh ultrapure water. In this morphology control, crystal defects change in ZnO nanorods need to be investigated. They are key factors for indirect, interband transitions of ZnO opto-electronic devices in visible light range. Taking their high energy and spatial resolution, using photoluminescence analysis and valence electron energy-loss spectroscopy in scanning transmission electron microscopy (STEM-VEELS), oxygen vacancy point defects are detected on the tip-edge of a tapered nanorod. They serve as an opto-electrical hotspot for the light-driven formation and tunability of the opto-electrical properties. A double increase of electron energy absorption on near band edge energy of ZnO was observed near the tip-edge of tapered nanorod.

Chapter 5 concludes with lessons learned in this thesis. Additional future work is presented: optical properties study by cathodoluminescence, and antimicrobial effects by CuO nanoflowers. Overall, this thesis have opened new perspective of transition metal oxide crystallites fabrication using SPSC.