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# Defect-related photoluminescence properties of as-synthesized and annealed NiO nanostructures via hydrothermal method

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ABSTRACT

A hydrothermal-based synthesis technique was used to produce both amorphous and nano-grained NiO nanowires. The scanning electron microscopy images showed the morphologies before and after annealing treatment at 350 and 400 °C for 2 h. The microstructural features of the mixed amorphous and local crystalline in as-synthesized NiO and polycrystalline in annealed NiO were characterized by X-ray diffraction, transmission electron microscopy, and high-resolution transmission electron microscopy, respectively. The corresponding elemental compositions were determined via energy-dispersive X-ray. In addition, annealing-dependent effects on the photoluminescence spectra were observed in at least two different energy band regions, e.g., at ~395, 660, and 680 nm. The photoluminescence properties, including intensity and energy, of the individual NiO nanowires varied significantly with microstructural changes arising from nickel and oxygen defects from annealing the as-synthesized amorphous NiO. The microstructural and optical origin of as-synthesized amorphous and annealed nano-grained NiO nanowires is discussed on the basis of the aforementioned results.



## 1. Introduction

Among the numerous transition metal oxides, nickel oxide (NiO) is one of typical p-type semiconducting materials possessing a wide bandgap (3.6–4.0 eV) [1]. Most NiO-based nano-structures have multiple oxidation states (e.g., NiO [2], $NiO_2$ [3], $Ni_2O_3$ [4], $Ni_3O_4$ [5], and $NiO_4$) and have received significant attention owing to their various applications in science and technology, such as electrochromic display devices [6], chemical sensors [7], solar cells [8], and catalysts [9]. These nanostructures have been synthesized through a variety of methods including sol–gel [10], spray pyrolysis [11], sonochemistry [12], solid-state reaction [13], and microemulsions [14]. However, these strategies have drawbacks stemming from complex processes, high-energy consumption, low-yield, long reaction time, prohibitive costs, and low purity. Owing to the simple process, low-cost, and high purity compared with that of other approaches, the hydrothermal method is a promising technique for synthesizing metal-oxide nanostructures. Recently, Xiong et al. [15] synthesized mesoporous NiO with various hierarchical nanostructures at temperatures of 140–180 °C for use in supercapacitors. Li et al. [16] also used a hydrothermal route at temperatures below 200 °C to synthesize vertically aligned and interconnected two-dimensional (2D) nickel oxide nanowalls via a template-free approach. In addition, Paravannoor et al. [17] used a simple hydrothermal method to synthesize porous thin film NiO nanowires for use as electrodes in supercapacitor devices. Although a variety of NiO nanostructures have been realized by the hydrothermal technique as above, only few studies demonstrate a correlation between the crystallography and/or surface and optical performances like photoluminescence. Especially, it is noticeable that most of results about the ultraviolet/visible ratio of NiO nanostructrues reveal a value less than 1 [18–20] due to the non-stoichiometric elemental composition such as nickel or oxygen defects. Therefore, it will be very important to optimize the NiO nanostructures for our needs. In this work, NiO nanostructures were synthesized via hydrothermal processes with the post-annealing treatment, among process variables such as the reaction temperature [21], duration [21], reactant concentration [22], and applied templates [23], to enhance the ultraviolet/visible ratio. Especially, we found the proper synthetic NiO condition for the highest aspect ratio (~1050) from previous research [21]. Hence, we chose the same hydrothermal reaction temperature and time for optical properties instead of gas-sensing properties [21]. However, we tried to enhance the PL properties of NiO nanowires with the different annealing temperature zones (350 °C and 400 °C) causing the change of preferred orientation and stoichiometry of NiO nanostructures. In addition, the microstructural conversion of NiO nanowires with/without post-annealing were examined through both SEM and TEM microscopic analyses. Furthermore, their microstructural and optical properties were investigated.

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## 2. Experimental

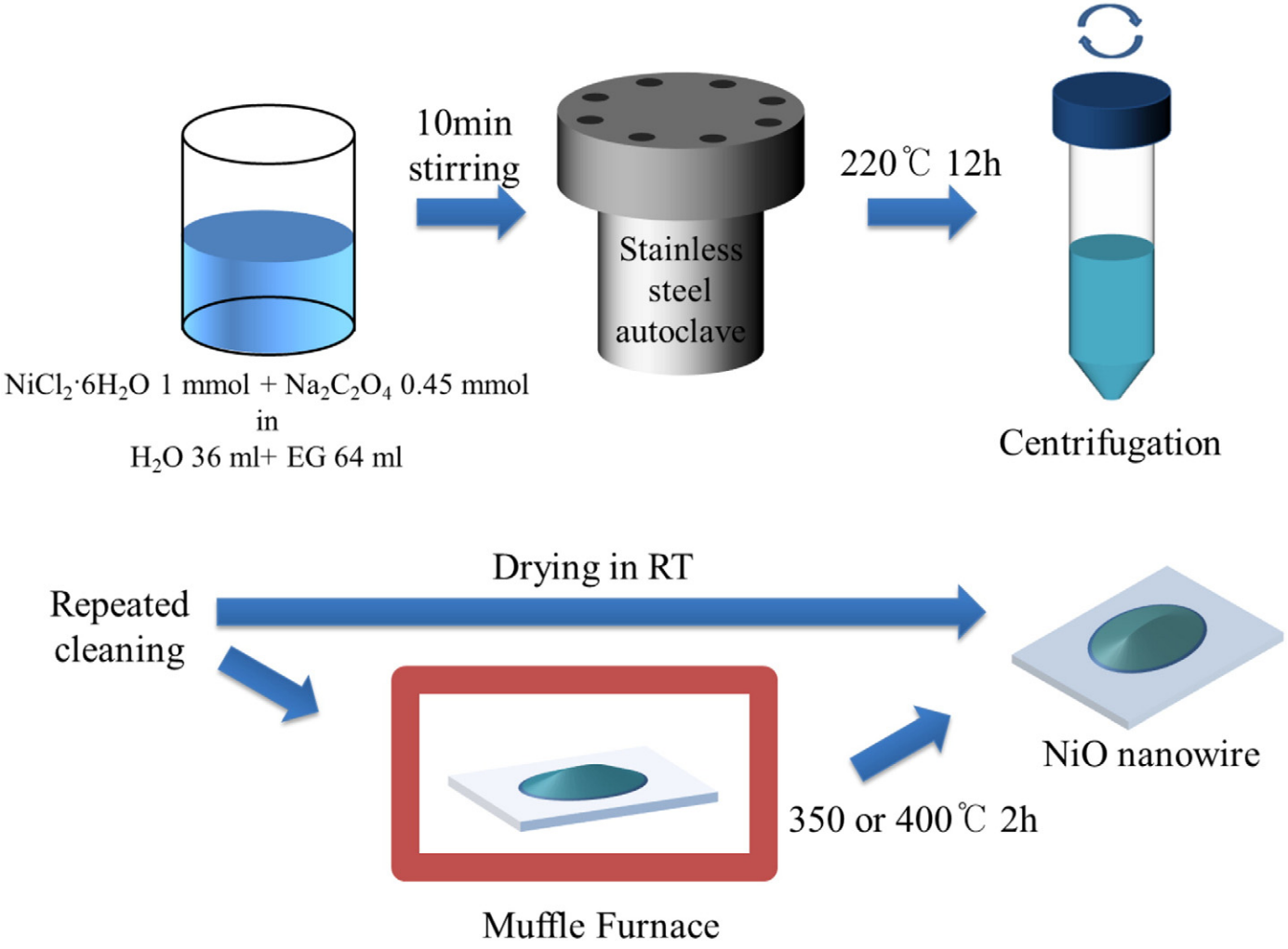
As scheme 1 shows, 1 mmol $NiCl_2 \cdot 6H_2O$, 0.45 mmol $Na_2C_2O_4$, 36.0 ml $H_2O$, and 64.0 ml ethylene glycol were mixed in a 200 ml beaker. After 10 min of stirring, the mixed solution was transferred to a 200 ml teflon container and autoclaved at 220 °C for 12 h (h). The temperature of the autoclave was brought to room temperature. The precipitates were collected by centrifugation and then washed repeatedly with deionized water and ethanol, thereby resulting in the as-synthesized blue-green NiO products. These products were subsequently heated to 350 and 400 °C and maintained for 2 h in a furnace in order to determine the effect of annealing on their morphology and structure. The samples assembled NiO nanoparticles were then collected.

The morphologies of the as-synthesized and annealed NiO products were characterized using scanning electron microscopy (SEM, Hitachi S-4200 (1997), 20 kV) and transmission electron microscopy (TEM, Phillips CM-200 (1997), 200 kV). In addition, X-ray diffraction (XRD) with a glancing angle of 0.5° (X'pert MPD, Philips, with Cu-$K_\alpha$ radiation) and an energy-dispersive X-ray (EDX) spectrometer attached to a TEM were used to determine the crystalline structures and composition of the individual products. The microstructural characteristics of the pre- and post-annealing products were thoroughly compared by examining high-resolution TEM (HRTEM) images and selected-area electron diffraction (SAED) patterns. Furthermore, the corresponding defect-related optical properties were determined at room temperature via photoluminescence (PL) measurements performed using a SPEC-1403 PL spectrometer (Kimon, 1 K, Japan) equipped with a 325 nm He-Cd laser source.

## 3. Results and discussion

Fig. 1 shows the SEM images of as-synthesized and annealed NiO products, respectively. The SEM images in Fig. 1(a-b) indicate that the as-synthesized NiO nanowires have approximate diameters and lengths of a few tens of nanometers and a few hundred microns, respectively. These bundles were formed possibly through a sequence of (1) nucleation, (2) surface-regulation, (3) growth, and (4) oriented attachment [24] and resulted from the strong van der Waals attraction [25] between the individual nanowires. In addition, there are no significant morphological differences between as-synthesized NiO (Fig. (a–b)) and 350 °C-(Fig. (c–d)) and 400 °C- (Fig. (e–f)) annealed counterparts.

The effect of annealing on the structure of the aforementioned materials was examined by the XRD patterns (Fig. 2). Generally, the stoichiometric NiO nanostructures originating from $Ni^{2+}$ and $O^{2-}$ collisions could be formed under higher temperature (> 300 °C) [26]. Therefore, the annealing temperatures of as-synthesized NiO were performed at 350 °C and 400 °C, respectively, for sufficient electrostatically neutral. As Fig. 2(a) shows, the (200) and (220) lattice planes constitute the main peaks in the pattern of the as-synthesized NiO; the appearance of these strong peaks, in the same positions, in the cases of the 350 °C (Fig. 2(b)) and 400 °C (Fig. 2(c))-annealed materials, suggests that




**Scheme 1.** Schematic of individual hydrothermal steps for synthesizing amorphous and nano-grained NiO nanowires.