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ScienceDirect

Procedia Chemistry 19 (2016) 125 – 132

Procedia Chemistry

5th International Conference on Recent Advances in Materials, Minerals and Environment (RAMM) & 2nd International Postgraduate Conference on Materials, Mineral and Polymer (MAMIP), 4-6 August 2015

Electronic properties of ZnO nanoparticles synthesized by Sol-gel method: A LDA+U calculation and experimental study

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Abstract

ZnO nanoparticles were prepared by sol-gel storage method to determine the optimum growth time. The precursor was zinc acetate dihydrate and methanol used as solvent. NaOH act as additive that changes the initial sol pH. The stabilize growth of ZnO nanoparticles was recorded after 12 hours aging time. Structural characterization revealed a single phase of ZnO with hexagonal wurtzite structure. Absorption spectra showed the synthesized ZnO nanoparticles exhibit an optical absorption in visible region. In addition, a systematic computational method within density functional theory frame work was used to elucidate the electronic properties of the synthesized ZnO nanoparticles. Calculations were performed using local-density approximation corrected by Hubbard U method. Hubbard U allowed the alteration of electronic state energy of Zn and O which improved the calculation. The calculated energy band gap demonstrates a value close to experimental data.

Peer-review under responsibility of School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia

Keywords: ZnO nanoparticles; density functional theory; sol-gel; electronic properties

Peer-review under responsibility of School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia
doi:10.1016/j.proche.2016.03.125

Nomenclature

LDA Local density approximation
LDA+U Local density approximation with Hubbard U correction

1. Introduction

Over decades, rapid increase in number of research on ZnO has been marked. The great attention has risen due to its unique properties especially wide band gap energy (3.37 eV at ambient temperature) and large binding energy (60 meV). The wide band gap offers the electronic transition to occur down to visible light region. Also, the binding energy persist the event of excitonic absorption and recombination between electron and hole even at room temperature[1]. This process is enhanced with the nature of a direct type band structure that improved the efficiency of photo-generated electron transfer[2]. These properties serve as significant criteria in fabricating optoelectronic devices, such as lasers, photodiodes, and solar cell[3-5].

The formation of high purity ZnO nanoparticles is essential as it affect the resulting electronic properties. Various synthesis techniques have been applied to produce ZnO nanoparticles. Starting from high temperature synthesis protocol such as chemical vapor deposition and hydrothermal process, a wet chemical phase is also employed[6, 7]. Sol-gel method is a simple yet convenient technique that able to produce ZnO nanoparticles with preferred morphology and sizes. The ability to control hydrolysis and condensation rate has made sol-gel method relatively versatile[5].

Often, the first-principles calculation is used to elucidate the properties of ZnO. This technique facilitates the understanding of the ZnO behavior because they involved the calculation of the ground-state energy of the system by means of density functional theory (DFT). Several works has employed DFT with local density approximation (LDA) as the exchange-correlation functions [8, 9]. Due to drawbacks of LDA that underestimate the band gap of ZnO, the Hubbard U (or LDA+U) approach has been used[10]. However, the works involving the prediction of the electronic and optical properties from experimental input are still limited. The effort of correlating both experimental and physical models is essential in order to better explain the properties of synthesized ZnO nanoparticles.

In real situation, the ZnO nanoparticles are expected to be produced soonest possible. Thus, time has become the key factor. This work aims to study the stability of ZnO growth by means of shortest sol aging time. The quality of synthesized ZnO is then tested through structural and morphological characterization. The absorption spectra of ZnO nanoparticles are also examined. Also, the calculated results from first-principles method are compared and used to explain fundamental behavior and compliment experimental data.

2. Methodology

2.1 Synthesis of ZnO nanoparticles via sol-gel storage method

The ZnO sol was prepared by mixing 0.2 M zinc acetate dihydrate [Zn(CH3COO)2.2H2O] and 200 mL of methanol (CH3OH) at room temperature. The solution was stirred for 2 hours until a clear solution was obtained. A 1.0 M NaOH was later titrated into the solution until the pH reached pH 9. At this stage, the clear solution has transformed into milky white slurry. The resulted white slurry was stirred for another 1 hour to allow a homogeneous mixing. After that, the sample was left alone for 12 and 24 hours to allow the complete hydrolysis and gelation. The aged samples were then showing separation between a clear solution and white precipitate that sediment at the bottom of the storage bottle. Filtration process was the carried out to obtain the white precipitate and further dried in an oven at 1β0 ˚C for β hours. The dried samples were ground with mortar and pestle to yield ZnO powder. Finally, the powder was calcined at θ00 ˚C in normal air to produce a well crystallize ZnO nanoparticles. Morphological characterization was done using field emission scanning electron microscope