Hydrothermal growth of ZnO on annealed electrodeposited titanate film: Influence of zinc nitrate and methenamine

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Received 18 November 2006; received in revised form 21 February 2007; accepted 28 February 2007
Available online 7 March 2007

Abstract

Hydrothermal growth of hexagonal ZnO nanorods on the annealed titanate nanotube films is reported as a function of molar ratio of Zn(NO₃)₂ and methenamine (1:1–1:4). The molar ratio of 1:4 results in a dense and thinner rod in comparison with other molar ratios. Corn-like structures of the rods are believed to be due to the higher amine concentration. Raman peaks at 437 and 331 cm⁻¹ are assigned to E₂ and E₂₉̅₁-E₂₉̅₄ modes. Near band gap edge and green photoluminescence emission indicates the structural and oxygen vacancy. O₁s peak is found built-up of sub-peaks at 530.62, 531.8 and 532.84 eV corresponding to O²⁻ on normal wurtzite structure and OH and oxygen vacancies of ZnO, respectively.

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PACS : 45.20.dh; 77.84.Dy; 73.40.Sx; 81.07.—b

Keywords: DSSC; Titinate seed; ZnO; Hexagonal nanorods

1. Introduction

In case of dye-sensitized solar cells (DSSC), formation of space charge via recombination of photo-injected electrons is a difficult task indicating higher recombination rate due to the absence of an energy barrier at the electrode/electrolyte interface [1,2]. The high recombination rate can be reduced by use of bilayer electrode, composite semiconductor electrode and so on [3–5]. The recent trend in the development of DSSC therefore focuses on the use of composite materials such as ZnO/TiO₂ [6], ZnO/SnO₂ [7], CdS/MgO [4], etc. Because of the interesting effects of size and quantum confinement, many efforts are devoted to grow various nanostructures of ZnO, which has received much attention owing to its band gap energy close to TiO₂. Even though, nanocrystalline TiO₂ reduces the recombination rate by forming an energy barrier at the electrode/electrolyte interface, still the conversion efficiency needs to be improved. Rajaram et al. have studied the composite TiO₂/ZnO using layer-by-layer method for DSSC, where they observed that this composite further reduces the recombination rate [6]. The reduction in the recombination rate is due to the reduction in the charge transfer rate of TiO₂/ZnO composite thereby increasing the photocurrent. Larger electron injection driving force and consequently a large photocurrent (Iₚₒ) can be obtained by lowering the charge transfer resistance. The material parameters such as grain size, porosity, surface area, amount of dye absorption, etc. affects the overall cell performance. Therefore the key issue for such DSSC; based on composites; is the synthesis of composite.

Few synthesis methods, including vapor deposition, template-assisted method, and hydrothermal method, have been reported for the synthesis of ZnO nanostructures [8–13]. Amongst these, the hydrothermal method is the simple, economical, low temperature growth and large-scale production method. Till date, the known method, to grow ZnO nanomaterials on a substrate using hydrothermal route is based on the use of an aqueous solution containing zinc salts, and/or organic amines [14–17]. For the aligned ZnO nanorods on the substrate, the Zn-derived thin films (Zn and ZnO film, textured ZnO nanocrystal) are used as a seed layer [15–18]. Although many reports are available for the growth of ZnO nanostructure...