



Synthesis of galaxite, $\text{Mn}_{0.9}\text{Co}_{0.1}\text{Al}_2\text{O}_4$, and its applications a novel nanocatalyst for electrochemical hydrogen evolution reaction

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ABSTRACT

A new compound $\text{Mn}_{0.9}\text{Co}_{0.1}\text{Al}_2\text{O}_4$ nanowires were synthesized by thermal method. The resulting powder samples were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD). We found that a set of phase transformation occurred during the process. Eventually, five phases including three spinel phases, the corundum ($\alpha\text{-Al}_2\text{O}_3$) and MnO were formed at 1100°C . As dominant morphology, the cubic galaxite nanowires were identified by X-ray analysis.

Moreover, X-ray analysis showed that Mn_3O_4 and Co_3O_4 nanoparticles were formed in tetragonal and cubic symmetry respectively. The SEM image revealed that a dominate morphology of product has cubic nanowires shape with an average diameter in range 38–43 nm. Furthermore, we observed that influence of temperature was very important in the nanowire formation process. Electrochemical hydrogen evolution reaction (HER) of synthetic composite was evaluated and the over potential of HER was calculated about 110 mV with low Tafel slope equal to 42 mV dec^{-1} , which was comparable with amounts reported transition metal dichalcogenides with satisfying durability.

1. Introduction

During the past decade, constructing quasi-1D nanostructure and one-dimensional materials have attracted much interest due to their enriched properties and potential applications in electronics, spintronics, optics and etc. [1–5]. Moreover, Metal oxide nanowires are versatile nano-structured materials with diverse unique properties. Hence, many techniques have been developed recently for the synthesis of such nanostructure materials. For example, Lee et al. studied systematically technique oxide-assisted growth [6], and also semiconducting oxide nanobelts were fabricated by evaporating the appropriate commercial metal oxide powder [7]. Lately, metal oxide nanowires consist of low-melting-point metals were successfully synthesized by direct heating the metal powder in a tube furnace [8]. Due to nanometer-size wires, rods, and tubes of metals were always the center of study of one-dimensional nanomaterials, electro-chemical deposition [9], Sol–gel

deposition [10], chemical vapor deposition and chemical polymerization deposition have been employed as major template-synthesis methods [11]. Among the various methods for preparing nanomaterials, one of the simplest methods is annealing method.

Herein, we reported the synthesis of galaxite novel compound $\text{Mn}_{0.9}\text{Co}_{0.1}\text{Al}_2\text{O}_4$ nanowires by the thermal method. Additionally, we observed that a set of phase transformation were occurred during the process. The other part of the product is nanoparticles including two spinel phases Mn_3O_4 , Co_3O_4 and corundum ($\alpha\text{-Al}_2\text{O}_3$). Entirely, all the obtained lattice constants were in accordance and on the agreement with the previous reports.

Rapid human population growth, related fossil fuel crisis and destructive effects for the environment are the factors that encourage human using renewable and green energies is a suitable replacement for fossil fuel have been regarded recently nowadays one of the most important concerns in the energy field is converting energy of hydrogen

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to electrical energy in the form of hydrogen fuel cells [12,13].

Platinum has always been known as an important catalyst for producing and releasing the power hydrogen, which was unfortunately expensive and scarce [14].

Two dimension compounds known as transition metal dichalcogenides like MoS_2 , WS_2 and NixSy have been widely investigated in the literature [15]. Furthermore, for hydrogen evolution reaction doping cobalt nanoparticle have been studied. For achieving the better results due to electrocatalytic activity, it should impose some defects to these compounds [16–18]. Dichalcogenides despite their good electroactivity, have poor electrical conductivity as well the insufficient active sites in the edge of the layers [19].

All the efforts that can be done for increasing the electrical conductivity in two-dimensional dichalcogenides should facilitate the electron transfer to electro active sites [19,20]. In this regard synthesis, the composites hybrids via introducing the metals during the synthesis

process can promote the conductivity and electroactivity.

In the following, the hydrogen evolution reaction (HER) properties of prepared galaxite $\text{Mn}_{0.9}\text{Co}_{0.1}\text{Al}_2\text{O}_4$ nanowires was investigated by linear sweep voltametry (LSV) and electrochemical impedance spectroscopy (EIS) methods and the results were evaluated by over potentials and Tafel slopes. Overall promising HER properties was inferred from the results.

2. Experimental procedure

The sample was prepared by mechanical alloying of Mn, Co and Al powders taken with the stoichiometric ratio. The sample was annealed at 1100°C for 72 h and cooled down to 630°C in a furnace. The alloy was kept for 68 h at this temperature and finally cooled down gradually to room temperature. All the process was done in argon atmosphere. The morphology of the nanostructures was investigated using scanning electron microscopes (SEM) (XL30, Philips, Netherlands) and energy-

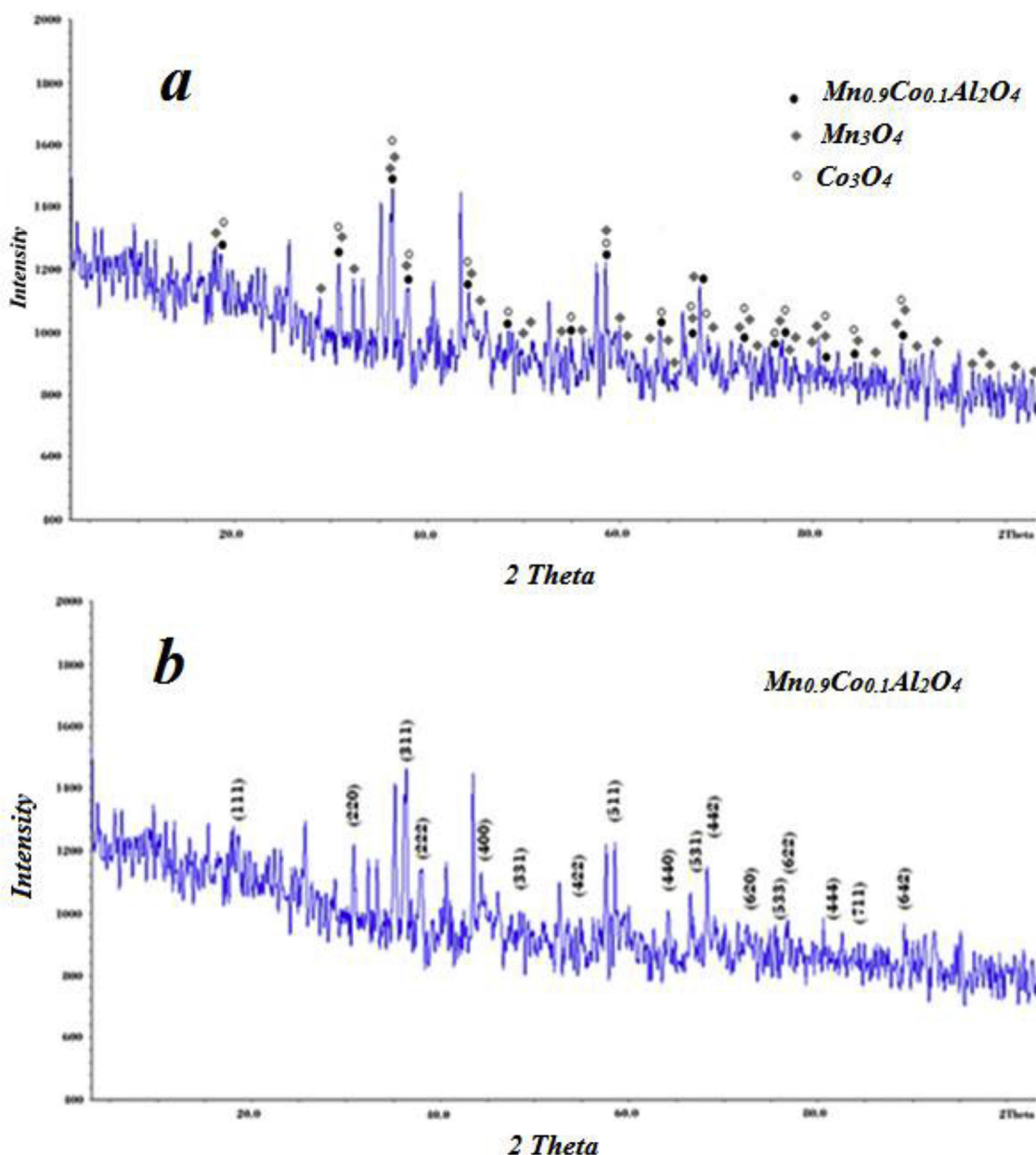


Fig. 1. XRD pattern exhibiting (a) $\text{Mn}_{0.9}\text{Co}_{0.1}\text{Al}_2\text{O}_4$ nanowires with Co_3O_4 and Mn_3O_4 nanoparticles at room temperature, and (b) Bragg sheet for galaxite compound of $\text{Mn}_{0.9}\text{Co}_{0.1}\text{Al}_2\text{O}_4$ nanowires.

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