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Short Communication

Controlled synthesis and electrochemical properties of Ag-doped Co_3O_4 nanorods

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ABSTRACT

Ag-doped cobalt oxide (Co_3O_4) nanorods were successfully synthesized using hydrothermal route at 90, 120, 150, and 180 °C. The face-centered cubic structure of Co_3O_4 was confirmed through X-ray diffraction pattern. A well-defined Raman active mode of vibrations ($E_g + F_{2g} + A_{1g}$) revealed the cubic Co_3O_4 formation. The morphology of Ag-doped Co_3O_4 nanorods was revealed from scanning electron microscopy images. High specific capacitance of 584 F/g at scan rate of 5 mV/s was obtained for the product synthesized at 150 °C. The improved oxygen evolution reaction (OER) for the synthesized materials was observed using linear sweep voltammogram, electrochemical impedance spectroscopy, and chronoamperometry. The obtained Ag-Co_3O_4 nanomaterials have more possibility to be adapted as OER catalyst for water splitting application.

Introduction

Generally, function and properties of materials depend on their compositions, crystal structures, size, and morphologies [1]. Among them, transition metal oxides grasp the attention of researchers by contributing the emerging potential applications and aiming for good comprehensive, surface reactive, and useful new designed functional materials [2,3]. The consumption of renewable energy is raised as an alternative energy to fossil fuels. Thus, energy storage is one of the important areas focused by the researchers for wind up the society with green [4]. Owing to this, water splitting is one of the most environmental friendly techniques for potential applications. Therefore, it is a suitable method to gain hydrogen in highly pure form and oxygen by electrolyzer. Even though the theoretical value of about 1.23 eV is good enough to start up the water oxidation process, in practical it requires high amount of energy, $\Delta G = 237.21$ kJ/mol, for overall reaction [5]. Due to this fact, researchers are working to

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reduce the over potential by controlling the processing parameters for tuning the morphology and by doping the foreign elements.

Nanosized cobalt oxide (Co_3O_4) is one of the most fascinating p-type environmental friendly semiconductor materials with low cost and highly commented materials for remarkable applications. It is also a fascinating technological material in hydrogen evolution reaction (HER), and oxygen evolution reaction (OER) [6]. The spinel Co_3O_4-based electrode material possesses high efficiency, long-term performance, and good corrosion stability to be used as an efficient electrocatalyst [7–9]. Though it possess many advantages, the physicochemical properties and the behavior of the nanosized material entirely enhanced by the doping process which is the most beneficial technique to induce and tune the material property. Many studies have been conducted to synthesize novel shapes in Co_3O_4 such as nanospheres, belts, rods, sheets, urchins, lowers, cubes, wires, platelets, and sheaf-like nanostructure [10–22].

This study presents the template-free one-pot hydrothermal approach to synthesize Ag-doped Co_3O_4 nanorods by controlling the processing temperature as 90, 120, 150, and 180 °C for electrochemical water splitting application. The fundamental characterization studies were conducted to confirm the formation of Ag-doped Co_3O_4 nanostructures (Supplementary Figs. S1–S6, Tables S1 and S2). Moreover, the electrochemical studies were carried out to investigate the electrochemical performance of synthesized Ag-Co_3O_4 nanostructures.

Materials and methods

Analytical-grade cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), 0.02 N silver nitrate ($AgNO_3$) solution, and urea (CH_4N_2O) were purchased from Sigma-Aldrich. Initially, 0.07 M $Co(NO_3)_2 \cdot 6H_2O$ and 0.03 M $AgNO_3$ solution were dissolved in 40 ml deionized water and mixed together under continuous magnetic stirring. Then, 0.2 M CH_4N_2O solution obtained by dissolving it in 80 ml of deionized water was poured into the earlier mixed solution drop wise under same stirring condition. This solution was maintained for homogeneous stirring of about 500 rpm for 30 min continuously and then transferred into 250 ml autoclave. The solution-contained autoclave was subjected to the furnace for 12 h at 90 °C. The obtained pale pink ash was centrifuged from the solution and was washed with deionized water and ethanol five times to remove all the residues, resulting in the product T1. The same procedure was followed for different processing temperatures such as 120, 150, and 180 °C, resulting in the products T2, T3, and T4, respectively. The obtained product was annealed at 450 °C for 3 h to attain the crystalline phase.

Results and discussion

Phase, purity, crystalline nature, and crystallite sizes of the product were investigated using X-ray diffraction (XRD) data. Fig. 1 (a)–(d) shows the XRD patterns of Ag-Co_3O_4 nanostructures, which indicate the formation of face-centered

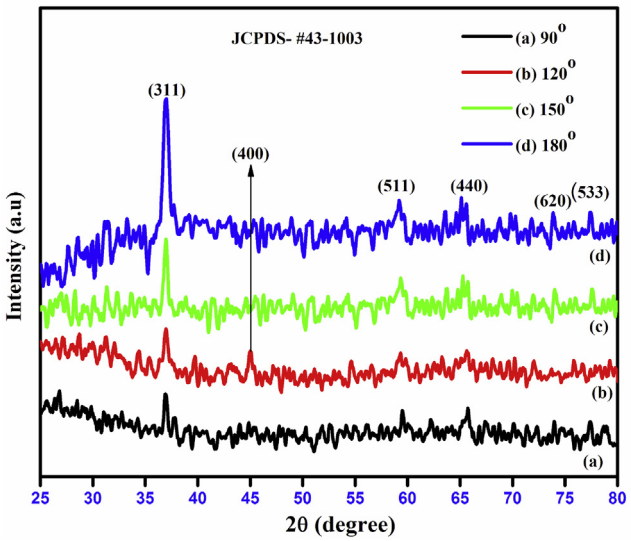

Fig. 1 – XRD pattern of Ag doped Co_3O_4 nanostructures a) 90° b) 120° c) 150° d) 180 °C.

cubic Co_3O_4 structure [23,24]. The diffraction peaks observed at 2θ values of 36.8°, 44.8°, 59.2°, 65.2°, 73.7°, and 77.3° correspond to the crystalline planes (311), (400), (511), (440), (620), and (533), respectively, which perfectly coincide with the standard JCPDS data card no #43-1003. No other impurity peaks are noticed in the XRD pattern of Co_3O_4. From the XRD spectrum, it is observed that as the processing temperature is increased to 90, 120, 150, and 180 °C, the first maxima of the products also increases. The average crystallite size was calculated using Debye–Scherrer formula:

$$D = 0.9\lambda/\beta \cos\theta \quad (1)$$

where λ is the X-ray wavelength, β the full width at half maximum intensity, and θ the Bragg's angle. The average crystallite size of the obtained product is 18.81 nm, as shown in Table S1 (see Supplementary). The lattice constant for each peak of the sample was calculated using the following formula:

$$a = d\left(h^2 + k^2 + l^2\right)^{1/2} \quad (2)$$

where h, k, and l are Miller indices of the crystal planes. The average lattice constant value obtained from the XRD result is 0.8092 nm, which perfectly coincides with the lattice constant value of standard JCPDS card #43-1003 for face-centered cubic Co_3O_4.

Fig. 2 (a)–(d) shows the observed SEM images in 1-μm scale with 20 KX magnifications of Ag-doped Co_3O_4 nanostructures. To investigate the optimum condition for synthesizing the good Ag-Co_3O_4 OER active catalyst, the processing temperature maintained inside the autoclave was explored as 90, 120, 150, and 180 °C. At 90 °C, the Ag-CoOOH units might be aggregated with diverse morphology and vastly agglomerate each other (Fig. 2a). At 120 °C, the possibility of nanorods formation with uneven length and width was high (Fig. 2b). At 150 °C, some of nanorods tend to merge together to form nanoplates due to the elevated temperature and pressure condition (Fig. 2c). Further, this optimal condition was more

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