Slot-die printed Co$_3$O$_4$ nanolayers

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Abstract. In this paper, we report on the possibility of obtaining uniform cobalt oxide nanolayers by slot-die printing of the dispersion onto conductive substrates. Dispersions for printing were obtained as a result of ultrasonic treatment of a mixture of cobalt oxide nanopowder with water. Nanopowder was synthesized by wet chemistry followed by heat treatment at a temperature of 200 ºC. The resulting powder has platelet morphology. The chemical composition, uniformity, structure and size of the powder and nanolayers of cobalt oxide were studied using X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray microanalysis (EDX). The proposed easy and cost-effective method of slot-die printing from dispersion can be prospectively used to the production of cobalt oxide nanolayers for development of thin-film electronics and solar cells.

1. Introduction

In recent years, a huge part of scientific research is aimed at improving the environmental situation in the world. One of the main dangerous factors for the environment is to generate electricity by burning fossil fuels. Finding new and developing existing alternative energy sources will reduce the amount of harm to nature. One of the best options for alternative energy sources is the use of photovoltaic technology to convert solar radiation into electricity. At the same time, when searching for alternative fossil fuels, you must consider the cost of new technologies. Based on these criteria, the most promising alternative energy source is perovskite solar element, since it has a relatively low cost and high development rates. However, the instability of perovskite solar element is a significant disadvantage and limits its use on industrial scale.

Usually perovskite solar element is collected from two electrodes between which are active layer perovskite and layers for transfer of electrons and holes. Improvement and development of new transport layers is the main option of solving instability of perovskite solar element. In addition, the use of the appropriate hole-transport layer can improve the efficiency of the transformation of sunlight into electrical energy. The main criterion for selecting material for the hole-transport layer is the value of its prohibited zone, which should reduce the barrier between perovskite layers anode [1, 2].

One of the promising materials for the hole-transport layer is cobalt oxide. This material has a suitable prohibited zone (~ 5.3 eV), high conductivity and heat resistance, environmental and environmental resistance [3-5]. Currently existing methods of obtaining holes-transport layers based on cobalt oxide cannot be implemented on an industrial scale, as they are costly or require large energy costs. In this regard, the purpose of this scientific work is to develop the method of obtaining Co$_3$O$_4$ nanolayers for use in perovskite solar elements, which will solve the problems described above.
2. Materials and Experimental Methods

The production of cobalt oxide nanolayers occurs consistently in two stages: synthesis of nanoparticles and applying dispersion on substrate. First, prepare a solution of 1M CoCl$_2$·6H$_2$O (cobalt chloride) and 2M NaOH (sodium hydroxide) for obtaining Co(OH)$_2$ (cobalt hydroxide). Mixing of solutions occurs with constant mixing, using magnetic bag. The process is completed when pH=10 is reached. To determine the pH solution is used pH-meter. The resulting blue-green sediment is filtered and washed with DI-water at least three times. After which the precipitation is sent to drying in the coupling furnace all night at 80°C. The obtained hydroxide cobalt is crushed and subjected to thermal treatment in the coupling furnace at 200°C within 2 hours. Nanopowder Co$_3$O$_4$ mixed with DI-water (H$_2$O) with 5 mg/ml concentrations and affected ultrasound for 1 min with subsequent centrifugation (5 min, 3500 rpm/min). The obtained dispersions were applied to pre-purified substrates of glass with ITO coating by the slot-die printing method. The printing temperature is 80°C. One pass of the printed head is applied one layer of cobalt oxide. Substrates were cleaned with consistent ultrasound effect within 15 minutes in three different environments. X-ray diffraction phase analysis (XRD) was carried out by means of Diphre 401 at CrKα-radiation using Crystal-morphic database JCPDS. The definition of the chemical company of the nanopowder formed during temperature processing was carried out using the scanning electron microscope (SEM) "Vega 3SB" (Tescan) with an energy-dispersive X-ray microanalysis spectrometer (EDX) INCA x-act (Oxford Instruments). The Ramman - spectroscopy was produced using the DXR Raman -spectrometer "Thermo Fisher Science" (USA). The control of the size of the cobalt oxide particles was carried out using the analyzer of the size of particles Zetasizer Nano ZS.

3. Results and Discussion

Figure 1 shows X-Ray of synthesized powders before and after thermal treatment to confirm the necessary phase. Registered diffraction peaks of the original powder are indexed on hexagonal symmetry phase Co(OH)$_2$ (JCPDS file № 30-0443). The X-Ray powder after thermal treatment corresponds exclusively to the structure of cubic spinel Co$_3$O$_4$ (JCPDS file № 42-1467, spatial group: Fd-3m). Diffraction peaks at 2θ = 19°, 31°, 36°, 38°, 44°, 55°, 59°, 65°, 68°, 74°, 78° grille plane (111), (220), (311), (222), (400), (331), (422), (511), (440), (531), (442), (620) accordingly. X-Ray confirm for full transformation Co(OH)$_2$ in Co$_3$O$_4$, without any additional phase.

![Figure 1. XRD of synthesized powders before and after heat treatment.](image-url)
Based on the analysis of the size distribution of \( \text{Co}_3\text{O}_4 \), the method of obtaining dispersion using centrifugation was selected. Particles are characterized by a narrow size distribution with an average size of \( 58.7 \pm 30.1 \) nm. The largest particle size does not exceed \( 120 \) nm.

**Table 1.** Size distribution of particles under addition influence.

| №№ | Kind of influence | Size distribution |
|-----|-------------------|-------------------|
| 1   | -                 | 87.5 ± 20.1       |
| 2   | Filtration        | 68.1 ± 30.1       |
| 3   | Centrifugation    | 58.7 ± 30.1       |
| 4   | US-barh           | 122.4 ± 20.8      |

Figure 2 shows microphotography with scanning electronic microscope for cobalt oxide powder obtained at \( 200 ^\circ \)C. The structure of the \( \text{Co}_3\text{O}_4 \) has a plate shape. This type of structure is characteristic for multi-phase \( \text{Co}_3\text{O}_4 \). The structure strongly affects the possibility of applying dispersion methods from the powder data.

**Figure 2.** Microphotography of \( \text{Co}_3\text{O}_4 \) nanopowder.

Raman - spectra were recorded to confirm the presence and phase composition of the \( \text{Co}_3\text{O}_4 \) nanolayers (Figure 3). Five Raman peaks are observed on the spectra at 194.2, 479.3, 521.2, 617, 688.6 cm\(^{-1}\), which correspond to phonon oscillations of single-phase \( \text{Co}_3\text{O}_4 \). When the number of layers increases, the intensity of the peaks decreases, which indicates a decrease in the size of the nanoparticles in the places where the spectra are removed.

**Figure 3.** Raman spectrum of \( \text{Co}_3\text{O}_4 \) nanolayers.
Based on the transmission spectra, a significant decrease in the average transmission value was found with an increase in the number of layers. Samples obtained by slot-die printing with five Co₃O₄ nanolayers have a transparency of less than 60% over the entire wavelength range. Such a low value may be due to surface quality, which may cause light scattering. This value of the film transmission is unsatisfactory, which may lead to a decrease in incident light and a decrease in the overall efficiency of the device. A sample with one nanolayer has a maximum transmittance value and may have an uneven substrate coating. It was decided that a sample with three nanolayers is optimal in terms of uniformity of the substrate coating and transmission. For samples with one and three nanolayers in the wavelength range from 500 to 550 nm, there is a reduction in transmittance of up to 70%, which is typical for Co₃O₄.

On microphotography from an optical microscope (Figure 4), it can be observed that the sample obtained by slot-die printing with one nanolayer has rare small clusters of nanoparticles. With increasing layers, the number of clusters increases, and their distribution becomes more uniform, which with a large number of layers can lead to the formation of a uniform dense film. These clusters with a sufficiently large size reduce sample transmission and may cause an increase in the device's resistance, which will lead to poor conductivity of the hole-transport layer.

![Microphotography of Co₃O₄ 1 - nanolayers (left) and 5 - nanolayers (right).](image)

Figure 4. Microphotography of Co₃O₄ 1 - nanolayers (left) and 5 - nanolayers (right).

Figure 5 shows microphotography from a scanning electron microscope for samples with five nanolayers. These nanolayers have a mesoporous morphology and a small number of agglomerated spherical nanoparticles of a larger size. Microphotography show that nanoparticles cover the entire surface of the substrate without forming visible holes.

![Microphotography of Co₃O₄ a sample with five nanolayers.](image)

Figure 5. Microphotography of Co₃O₄ a sample with five nanolayers.
On the energy-dispersive X-ray spectrum are observed cobalt, oxygen and a significant number of other elements characteristic of glass, that confirming the elemental composition of cobalt oxide agglomerates on the substrate. Figure 6 shows a multi-layer map of energy-dispersion spectroscopy, which suggests that Co$_3$O$_4$ nanolayers obtained by slot-die printing cover the entire surface of the sample.

![Figure 6. Map of energy dispersion X-ray spectroscopy.](image)

4. Conclusion
The proposed easy and cost-effective method of printing from dispersion makes it possible to form a uniform and dense cobalt oxide layer on the surface of substrates, which can be used prospectively in obtaining a hole-transport layer in perovskite solar cells.

References
[1] Ning Z, Fu Y and Tian H 2010 Energy and Environmental Science 3 1170–1181
[2] Jeon N J, Lee J, Noh J H, Nazeeruddin M K, Gratzel M and Seok S I 2013 Journal of the American Chemical Society 135 19087–19090
[3] Lee J H, Noh Y W, Jin I S, Park S H and Jung J W 2019 Journal of Power Sources 412 425–432
[4] Bashir A, Shukla S, Haur L J, Shukla S, Bruno A, Gupta D, Baikie T, Patidar R, Akhter Z, Priyadarshi A, Mathews N and Mhaisalkar S G 2017 The Royal Society of Chemistry 10 2341–2350
[5] Shalan A E, Oshikiri T, Narra S, Elshnawany M M, Ueno K, Wu H-P, Shi X, Diau E W-G and Misawa H 2016 ACS Applied Materials and Interfaces 8 33592–33600