Evolution of Cobalt Oxide Nanostructures on Glass Substrate via Two Step Solution Route Synthesis

A. R. Mariscal and M. C. Marquez

School of Chemical Engineering and Chemistry, Mapua Institute of Technology Manila Philippines, 0002
menandro.marquez@gmail.com

Abstract: Controlling the morphology in the nanoscale has proven to be an effective way to drastically change the properties of materials. In this study, several morphologies of cobalt oxide (Co3O4) were synthesized by employing a two-step solution route. A Co3O4 seed layer was first deposited on the glass substrate via spin coating using a cobalt acetate precursor followed by chemical bath deposition of another Co3O4 layer using cobalt nitrate precursor. The effect of the seed layer and the deposition times on the morphology of the secondary Co3O4 nanostructures was verified by employing scanning electron microscopy (SEM). Morphologies like nanoplatelets, nanorods, nanofibrils and porous nanowalls were observed in the SEM. Other characterization techniques such as Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction technique (XRD) were used to elucidate the formation of Co3O4. Furthermore, the surface of the seed layer was determined via atomic force microscope. It was found that the roughness of the seed layer ranges from ~0.3 to 3 nm depending on the concentration of the cobalt precursor used. Results showed that the morphology of Co3O4 can be easily modified using the two-step solution route technique. The alterations of the morphology of Co3O4 could lead to morphologies with unique properties and development of functional materials applicable in the field of energy and electronics.

1. Introduction

Cobalt oxide is a heavily investigated metal oxide due to its versatility in terms of applications. Cobalt oxide has attracted the interest of scientist in the recent decade for it has shown superb electrochemical properties which makes a viable material in the fields of batteries, electrochemical capacitors, electrochromic devices, gas sensors, as well as catalysts for oxygen reduction reaction [1-4]. Cobalt Oxide can be deposited in an electrode via successive ionic layer adsorption and reaction (SILAR), chemical spray pyrolysis, chemical vapor decomposition, solvothermal method, electrodeposition, chemical bath deposition, chemical combustion method, redox route, and pulsed laser deposition methods[5,6]. Cobalt oxide spinel nanostructures fabricated using the synthetic methods, yielded nanostructures with various morphologies such as nanotubes, nanowires, nanoplates, and nanoparticles[7]. Among these techniques, chemical bath deposition stand out due to certain advantages. Chemical bath deposition, or chemical solution deposition, is a preferred method since it has a low cost, simple design, great potential to scale-up, and produces high quality nanorods [8]. In this study, we reported the effects of seed layer, seed layer solution concentration, and growth time on the nanostructures formed. Nano sized crystalline metal oxides are preferred due to their large
surface areas, unusual adsorptive properties, surface defects and fast diffusivities [9,10]. Co₃O₄ is a material which may yield as a clean source of energy due to its capability as a catalyst for water splitting applications.

2. Methodology

Solutions were prepared using analytical reagent grade chemicals without further purification. Cobalt (II) acetate tetrahydrate from Sigma Aldrich was used as cobalt source for the seed layer. Cobalt nitrate hexahydrate and hexamethylenetetramine (HMTA) were used for the synthesis of the cobalt oxide nanostructures.

The substrates were prepared by cutting 5 mm x 15 mm glass slides using a diamond glass cutter. The glass substrates were then cleaned in ethanol, acetone, and distilled water, using a low frequency sonicator for 5 minutes each. This standard cleaning method was used to remove the grease and other contaminants on the glass substrates which may have been deposited during the cutting phase of the glass. Solutions of 0.03M, 0.04M, and 0.05M cobalt (II) acetate tetra-hydrate dissolved in methanol were prepared for the seed layer. The seed layer was deposited with aid of a spin coater. The glass substrate was attached to the coater and spun at 2400 rpm. The substrates were then annealed at 450 °C for 1 hour.

For the formation of the secondary nanostructures, 0.02M of cobalt nitrate hexahydrate and hexamine (HMTA) solution were used as precursors. Cobalt nitrate hexahydrate and hexamine (HMTA) were dissolved in deionized water with molar concentrations; and were sonicated for 30 minutes. The nanostructures were then grown onto the substrate via chemical bath deposition with temperature set at 90ºC. After growing, the substrate was washed with deionized water and then annealed at 450 °C for 1 hour.

3. Results and Discussion

3.1. X-Ray Diffraction

The diffractogram shows characteristic peaks which confirmed what the crystal structure of the synthesized material. The recorded peaks of the fabricated cobalt oxide seed layer and the cobalt oxide nanostructures grown on top of the seed layer confirmed this claim and corroborates with the standard JCPDS data (JCPDS card No: 073-1701) for cubic cobalt oxide (Co₃O₄).

The formation of Co₃O₄ seed layer (equations 1-3) and nanostructures (equations 4-6) using solution route technique can be summarized in the proposed chemical reactions presented below:

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\begin{align*}
\text{Co(CH}_3\text{COO)}_2\cdot 4\text{H}_2\text{O} + 2\text{NaOH} & \rightarrow \text{Co(OH)}_2 + 2\text{CH}_3\text{COONa} + 4\text{H}_2\text{O} \quad (1) \\
4\text{Co(OH)}_2 + \text{O}_2 + \text{H}_2\text{O} & \rightarrow 4\text{Co(OH)}_3 \quad (2) \\
\text{Co(OH)}_3 & \rightarrow (\text{annealed in air at 450 °C}) \rightarrow \text{Co}_3\text{O}_4 + \text{H}_2\text{O} \quad (3) \\
\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NaOH} & \rightarrow \text{Co(OH)}_2 + \text{NaNO}_3 \quad (4) \\
4\text{Co(OH)}_2 + \text{O}_2 + \text{H}_2\text{O} & \rightarrow 4\text{Co(OH)}_3 \quad (5) \\
\text{Co(OH)}_3 & \rightarrow (\text{annealed in air at 450 °C}) \rightarrow \text{Co}_3\text{O}_4 + \text{H}_2\text{O} \quad (6)
\end{align*}
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![Figure 1. XRD diffractogram of cobalt oxides (Co₃O₄) (from Cobalt (II) acetate tetrahydrate and Cobalt (II) nitrate hexahydrate precursors)](image-url)
3.2 Atomic Force Microscopy

Atomic Force microscopy (AFM) was employed to observe the surface roughness of the deposited seed layer and nanostructures. Based on the results; increasing the concentration of the solution leads to increase in the surface roughness of the seed layer. This surface roughness and concentration dependence is attributed to the increase in the Van der Waals forces between the particles which is due to less distance between particles if the solution is more concentrated\[11, 12\].

![Figure 2](image1.png)  \textbf{Figure.2.} Atomic Force micrograph of cobalt oxide seed layer with concentration of 0.03M 2D with reported roughness of root mean square of 0.383 nm.

![Figure 3](image2.png)  \textbf{Figure.3.} Atomic Force micrograph of cobalt oxide nanostructures with concentration of 0.03M with reported roughness of root mean square of 38.588 nm.

3.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to investigate the morphology of the seed layer as well as the influence of growth time and seed layer concentration on the nanostructures formed.

![Figure 4](image3.png)  \textbf{Figure.4.} Seed layers with concentrations A) 0.03M, B) 0.04M, and C) 0.05M.

With the SEM images of the seed layer there is an increase in number of particles as the seed layer concentration increase. This results in a rougher film, as confirmed by the AFM micrographs. Increasing the concentration of the solution, the presence of more cobalt oxide particles means that the distance between such particles is decreased. This causes the particles to agglomerate. Hence, more particles are present on the 0.05M seed layer compared to 0.03M seed layer. The diameter of the particles present in the seed layer film was not further investigated. The dark spots in the SEM images are not cobalt oxide particles; rather they are void undeposited spaces. It was noted that there are more dark spots present in the 0.03M SEM image as compared to the 0.05M seed layer.

![Figure 5](image4.png)  \textbf{Figure.5.} Nanostructures formed without seed layer, films that were grown at A) 0.5 hour, B) 1 hour, C) 3 hours.
Shown in Figure 3.5 are the SEM images of one step chemical bath deposition. As observed, there are not much nanostructures formed in this method. The only nanostructure that was present in the three samples, without seed layer, was nanosheets developing into nanoplates (Fig. 3.5., Image B). The nanosheets were parallel to the substrate and, as observed. There were no dot-like particles observed, unlike the ones present on the cobalt oxide seed layer.

**Figure 6.** Cobalt oxide nanostructures on seed layer with concentration 0.03M with varying growth times, A) 0.5 hour, B) 1 hour, C) 3 hours.

The above images show the evolution of cobalt oxide fibrils to cobalt oxide nanorods. These structures had the same seed layer concentration which was 0.03M. It was confirmed the formation of cobalt oxide nanorods using the same method in fabricating zinc oxide nanorods. From the images, the trend that was observed was that in the 0.03M fibrils and rods were common structures. Observing image B, the underlying layer has a different contrast compared to the underlying layer of the first image (image A). This shows that the nanostructure formed in image B is a tertiary formation. This means that given enough time, a nanostructure will form on top of a previously grown nanostructure.

**Figure 7.** Cobalt oxide nanostructures on seed layer with concentration 0.04M with varying growth time, A) 0.5 hour, B) 1 hour, C) 3 hours.

Nanowalls were the dominating structures on the 0.04M seed layer concentration. As seen on the image C, there is a difference in contrast between the underlying layer on the image compared to the top left and top right images. This also exhibits the same tertiary growth behaviour as stated observed in the previous images.

**Figure 8.** Cobalt oxide nanostructures on seed layer with concentration 0.05M with varying growth times, A) 0.5 hour, B) 1 hour, C) 3 hours.

A coral-like nanostructure was found on 0.05M seed layer concentration grew on 1 hour. It seems to grow perpendicular from the glass substrate. Other observed nanostructures that were grown on the 0.05M seed layer were nanosheets. Unlike the nanosheets found on the no seed layer samples, these nanosheets are perpendicular to each other. There were no trends observed. However, from these set of images it was found that there were nanosheets formed. It was proven that by depositing a seed
layer onto the glass substrate, it can modify the morphology of the cobalt oxide nanostructures. This is due to the elimination of the lattice mismatch between the nanostructures and the glass.

4. Conclusion
Nanostructures of Co3O4 have been synthesized using two step solution route technique. The effect of depositing a seed layer prior to the deposition of the secondary layer had been observed and was found to have a significant effect on the formation of various nanostructures; nanorods, nanowalls, nanoplates and nanofibrils. Though the temperature for the growth of these nanostructures is relatively low it was also observed that upon annealing it at 450°C for one hour could lead to the formation of Co3O4. This observation gives light to developing nanostructures at low temperature. Most importantly understanding the formation of various nanostructures by simply adding a seed layer could lead to synthesizing more complicated structures with unique or tailored properties for a particular application.

5. References
[1] Kuwabara T., Nishizawa B., Nakamura K., Ikeda Y., Yamaguchi T., Takahashi K.(2015). Electrocatalytic activity of electrodeposited cobalt oxide films to produce oxygen gas from water. Journal of Electroanalytical Chemistry 740 (2015) 14–20.
[2] Nguyen T.T., Nguyen V.H., Devasagiamani R.K., Kharismadewi D., Iwai Y., Shim J.J. (2016). Facile synthesis of cobalt oxide/reduced graphene oxide composites for electrochemical capacitor and sensor applications. Solid State Sciences 53 (2016) 71-77.
[3] Zhang H., Liu S. (2017). A combined self-assembly and calcination method preparation of nanoparticles-assembled cobalt oxide nanosheets using graphene oxide as template and their application for non-enzymatic glucose biosensing. Journal of Colloid and Interface Science 485 (2017) 159–166.
[4] Wang X., Yan C., Sumboja A., Lee P.S. (2013). High performance porous nickel cobalt oxide nanowires for asymmetric supercapacitor. Nano Energy (2014) 3, 119–126.
[5] Jagadale A.D., Kumbhar V.S., Lokhade C.D. (2013). Supercapacitive activities of potentiodynamically deposited nanoflakes of cobalt oxide (Co3O4) thin film electrode. Journal of Colloid and Interface Science 406 (2013) 225–230.
[6] Pudukudy M., Yaakob Z., Narayanan B., Gopalakrishnan A., Tasirin S.M. (2013). Facile Synthesis of Bimodal Mesoporous Spinel Co3O4 Nanomaterials and their Structural Properties. Superlattices and Microstructures 64 (2013) 15-26.
[7] Kung C.W., Chen H.W., Lin C.Y., Vittal R., Ho K.C. (2012). Synthesis of Co3O4 nanosheets via electrodeposition followed by ozone treatment and their application to high-performance supercapacitors. Journal of Power Sources 214 (2012) 91-99.
[8] Kim K.H., Umakoshi T., Abe Y., Kawamura M., Kiba T. (2015). Determination of effective growth time for zinc oxide nanorods using chemical solution deposition. Superlattices and Microstructures 88 (2015) 150-153.
[9] Manigandan R., Giribabu K., Suresh R., Vijayalakshmi B., Stephen A., Narayanan V., (2013). Cobalt Oxide Nanoparticles: Characterization and its Electrocatalytic Activity towards Nitrobenzene. Chemical Science Transactions 2013, 2(S1), S47-S50.
[10] Patil D., Patil P., Subramanian V., Joy P.A., Potdar H.S. (2010). Highly sensitive and fast responding CO sensor based on Co3O4 nanorods. Talanta 81 (2010) 37–43.
[11] Pourshaban E., Abdizadeha H., Golobostanforda M.R. (2015). ZnO Nanorods Array Synthesized by Chemical Bath Deposition: Effect of Seed Layer Sol Concentration. Procedia Materials Science 11 (2015) 352 – 358.
[12] You H.C. (2014). Transistor characteristics of zinc oxide active layers at various zinc acetate dihydrate solution concentrations of zinc oxide thin-film. Journal of Applied Research and Technology 13 (2015) 291-296.