Synthesis of Cobalt Oxide on FTO by Hydrothermal Method for Photoelectrochemical Water Splitting Application

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Abstract: Cobalt oxide thin films were successfully grown directly on fluorine-doped tin oxide glass substrates through a simple, green, and low-cost hydrothermal method. An investigation into the physicochemical characteristics and photoelectrochemical (PEC) properties of the developed cobalt oxide thin film was comprehensively performed. At various annealing temperatures, different morphologies and crystal phases of cobalt oxide were observed. Microflowers (Co3O4) and microflowers with nanowire petals (Co3O4/CoO) were produced at 450 °C and 550 °C, respectively. Evaluation of the PEC performance of the samples in KOH (pH 13), Na2SO4 (pH 6.7), and H2SO4 (pH 1) revealed that the highest photocurrent (~2.3 mA cm⁻²) was generated at ~0.5 V vs. reversible hydrogen electrode (RHE) for Co3O4 (450 °C) in H2SO4 (pH 1). This photocurrent corresponded to an 8-fold enhancement compared to the results reported by other studies. This promising photocurrent generation was due to the abundant source of protons, which was favorable for the hydrogen evolution reaction (HER) in H2SO4 (pH 1). The present study showed that Co3O4 is photoactive under acidic conditions, which is encouraging for HER compared with the mixed-phase Co3O4/CoO.

Keywords: cobalt oxide; mixed-phase; photoelectrochemical; water splitting

1. Introduction

Hydrogen (H2) is an ideal future energy carrier to replace fossil fuels. H2 can be extracted from water molecules through photoelectrochemical (PEC) water-splitting using direct solar energy, which has been actively studied globally [2,3]. Both components, water and sunlight, are abundant and available everywhere. PEC water-splitting requires a semiconductor material as a photoelectrode. This photoelectrode is exposed to sunlight and is the site for the initiation of the catalytic reaction. The results depend on the nature of the semiconductor. The n-type semiconductors, such as titanium dioxide (TiO2), act as a photocathode; the water molecule is oxidized to produce oxygen (O2) gas. Meanwhile, p-type semiconductors, such as Cu2O, act as a photoanode; the proton (H+) is reduced, and H2 is generated [4].

A few requirements need to be fulfilled by photoelectrodes to achieve an efficient PEC water-splitting process. The bandgap energy should be greater than 1.23 eV and less than 3 eV to allow the utilization of the spectral range of visible light [5]. To photoelectrochemically split the water molecule, the band edges of the photoelectrode need to be in straddle position to the water molecule redox potential, which means the conduction band (CB) of the material should lay at a more negative potential than the water reduction potential. Meanwhile, the valence band (VB) position should lay at a more positive potential to the...
water oxidation potential. Furthermore, a stable and highly photoactive photoelectrode is required to achieve an efficient PEC performance [6].

TiO$_2$ [7,8], Cu$_2$O [9], WO$_3$ [9], Fe$_2$O$_3$ [10], and perovskites [11] are among the semiconductor materials that have been extensively investigated as photoelectrodes, because these materials are highly abundant and require simple fabrication techniques and low-cost preparation processes. However, recently, cobalt oxide itself has also received considerable attention as a photocatalyst material. Cobalt oxide is attractive because of its suitable optical band gap of ~2.00 eV, which falls within the favorable band gap range for visible light absorption [9,12–15]. Co$_3$O$_4$ and CoO are reportedly the most stable phases of cobalt oxide and are the most investigated materials for PEC water-splitting applications [13]. Hong et al. (2017) reported that photocurrent densities produced by Co$_3$O$_4$ for PEC performance at −0.4 V bias vs. Ag/AgCl could be achieved at −0.50 mA cm$^{-2}$, approximately [9]. Liao et al. (2016) revealed that CoO can cleave water molecules without the addition of cocatalysts or sacrificial reagents. The photocatalytic process achieved ~5% efficiency of solar to hydrogen, which is the highest efficiency for a single material.

Cobalt oxide can be synthesized using various methods through a chemical or physical route [16]. The chemical route includes the sol–gel method [17], hydrothermal method [12], solvothermal method [18], cathodic reduction [19], and chemical vapor deposition (CVD) [20]. Meanwhile, a physical approach includes sputtering and physical vapor deposition (PVD) [19,21]. Cobalt (II) salts, such as cobalt (II) chloride hexahydrate, cobalt acetate tetrahydrate, and cobalt (II) nitrate hexahydrate are most used as starting materials [22,23]. The purity of the cobalt oxide phase depends on the preparation methods and the annealing temperature. The good crystallinity properties of Co$_3$O$_4$ thin films with preferred orientation along [111] direction were reported by El Bachiri et al. (2019) using spray pyrolysis technique of an aqueous solution of hydrated cobalt chloride salt. Prabaharan et al. (2017) synthesized Co$_3$O$_4$ nanoparticles by using a cheap and easy sol gel precipitation method producing nanoparticles agglomerated with spherical-shaped particles [24].

Cobalt oxide is a temperature-dependent material; when the cobalt compound is annealed at a low temperature with abundant air, Co$_3$O$_4$ is produced. In an adequate amount of oxygen, the Co$_2$O$_3$ changes to Co$_3$O$_4$ without any change in the lattice structure [25]. A cobalt compound forms CoO as the final product at a high annealing temperature (>900 °C) and under inert conditions [12,26,27]. In this study, the cobalt oxide thin film was directly grown on fluorine-doped tin oxide (FTO) glass through a hydrothermal method. The phase transformation of directly grown on the FTO will be studied based on the different annealing temperatures. We realize that the study of phase transformation directly grown on fluorine-doped tin oxide (FTO) glass through a hydrothermal method rarely been reported. The annealing temperatures of 450 °C and 550 °C were chosen based on our previous study on powder photocatalysts. The high crystalline Co$_3$O$_4$ produced at an annealing temperature of 450 °C was then transformed to mixed-phase Co$_3$O$_4$/CoO or pure CoO at higher temperature [12]. This study’s highest temperature was 550 °C because of the temperature limitation of FTO glass. The photoelectrode performance was then evaluated based on photocurrent generation, which reflected PEC water-splitting application’s response to an electrolyte.

2. Materials and Methods

2.1. Synthesis of Cobalt Oxide

Cobalt oxides were synthesized on FTO by a hydrothermal method according to a previous study [15]. Cobalt nitrate hexahydrate (2.90 g) with 99% purity from R & M Chemical, United Kingdom and urea (0.72 g) from Quality Reagent Chemical (QREC), Malaysia were dissolved in 50 mL of deionized water. Subsequently, the homogeneous solution was placed into a 100 mL volume autoclave made of stainless steel. The autoclaves were maintained at 100 °C for 6 h and naturally cooled to room temperature. Next, the thin film was rinsed with distilled water prior to annealing in N$_2$ gas at 450 °C and 550 °C for 3 h.
2.2. Characterization

The crystallinity of the sample was determined using X-ray diffraction (XRD) with Cu Kα radiation at a wavelength of 0.15406 Å (Siemens X-ray Diffractometer D5000, Munich, Germany). The surface morphology of the samples was observed using a field emission scanning electron microscope (FESEM) (JEOL JSM-7600F, Tokyo, Japan) and high-resolution transmission electron microscopy (HRTEM) (JEOL JEM-2100F, Japan). The optical properties of the samples were examined using a UV-Vis-NIR spectrophotometer (UV-3101PC Shidmadzu, Kyoto, Japan). Details of the chemical composition and binding energy were obtained with an X-ray photoelectron spectrometer (Fourier Kratos Analytical Axis Ultra DLD/2009, Manchester, UK).

2.3. Photoelectrochemical Measurement and Stability Test

Photochemical (PEC) measurements were performed with a three-electrode configuration that comprised the samples, saturated Ag/AgCl, and platinum as the working, reference, and counter electrodes, respectively. These cables were connected to a potentiostat (Versa stat, Ametex, Oak Ridge, TN, USA). To evaluate the effect of the pH of the electrolytes on the photocurrent generation, different solutions of 0.5 M KOH (pH 13), 0.5 M Na₂SO₄ (pH 7), and 0.5 M H₂SO₄ (pH 1) were prepared as the electrolytes. Prior to PEC measurement, the electrolytes were degassed with N₂ for 10 min. The photocurrent measurements were conducted under simulated solar light illumination at a power density of 100 mW cm⁻² with a Xenon lamp as the light source (ORIEL). Under similar conditions, Mott–Schottky data were collected under illumination at a frequency of 1000 Hz. The electrochemical impedance of the samples was evaluated using electrochemical impedance spectroscopy (EIS) by scanning from 1 Hz to 100,000 Hz using a similar potentiostat. The applied potential was converted into the reversible hydrogen electrode (RHE) scale using the Nernst equation; \( E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.05196pH + 0.1976 \).

3. Results and Discussion

3.1. Phase and Crystal Structure Analysis

The cobalt oxide thin film on FTO was fabricated using a sequential hydrothermal method and annealed under inert conditions. The product from the hydrothermal process that was not annealed (named as a pre-annealed sample) was also analyzed to confirm the first product produced by the hydrothermal method. XRD analysis was utilized in this study to fully understand the phase of cobalt oxide produced according to the annealing temperature. The XRD chromatogram in Figure 1 shows that cobalt (III) oxide (Co₃O₄) was formed on the FTO after the hydrothermal reaction (pre-annealed), as indicated by the diffracted peaks of (111), (220), (311), (511), and (440), which corresponded to the plane of the cubic crystal structure with the spinel Co₃O₄ phase (JSPD NO 00-042-1467). In addition, as the sample was later subjected to an annealing treatment of 450 °C, the intensity of the peaks belonging to the Co₃O₄ phase markedly increased, indicating an increase in crystallinity. Interestingly, at 550 °C, a mixed phase of Co₃O₄ and CoO was observed at approximately 36°, 45°, and 59°, indicating that oxidation of Co₃O₄ to CoO occurred. According to previous studies [28], increasing the annealing temperature decreases the amount of oxygen in the films, which might be explained by the increase in purity and crystallinity of the as-deposited Co₃O₄ (pre-annealed) and after annealing at 450 °C, and by the loss of oxygen in the form of water vapor during the annealing treatment.
Co$^{2+}$ species, respectively. For the Co 2p spectrum of the 550 °C thin film, the Co$^{3+}$ and Co$^{2+}$ spectrum of single-phase Co$_3$O$_4$ showed a clear image of weaker peaks compared with CoO was confirmed by the indication of a low appearance of satellites [31]. The Co 2p species were located at 777.07 and 778.95 eV, respectively. In addition, the presence of Co$^{2+}$ species was caused by water or solvent contaminant. A similar trend was also reported by Chen et al. (2020) on the annealing effect on MoS$_2$ [29]. The 2p$_{3/2}$ and 2p$_{1/2}$ peaks separation for both pre-annealed and annealed 450 °C samples are around ± 10 eV. According to H. Jadhav et al., between the 2p$_{3/2}$ and 2p$_{1/2}$ peaks, an energy difference of ~15 eV is characteristic of the Co$_3$O$_4$ phase [30]. The major peak in Co 2p$_{3/2}$ for the sample annealed at 450 °C de-convoluted into two peaks centered at 776.96 and 778.90 eV, which corresponded to Co$^{3+}$ and Co$^{2+}$ species, respectively. For the Co 2p spectrum of the 550 °C thin film, the Co$^{3+}$ and Co$^{2+}$ species were located at 777.07 and 778.95 eV, respectively. In addition, the presence of CoO was confirmed by the indication of a low appearance of satellites [31]. The Co 2p spectrum of single-phase Co$_3$O$_4$ showed a clear image of weaker peaks compared with that associated with CoO in the mixed phase of Co$_3$O$_4$/CoO [32]. Figure 2c shows the O 1s XPS spectra of the pre-annealed, annealed 450 °C, and annealed 550 °C samples. All samples produce oxygen peaks in different binding energy and height. The oxygen peaks of pre-anneal sample present at 529 and 530.6 eV. Meanwhile, the position oxygen peaks of annealed 450 °C and 550 °C samples are in lower binding energy, that is, at 527 and 528.6 eV. They differed only in the slight shifting in intensity and the peak position, thereby indicating that some oxygen atoms bind with different oxidation states of Co.

Figure 1. X-ray diffraction patterns of (a) the pre-annealed Co$_3$O$_4$, (b) the post-annealed Co$_3$O$_4$ at 450 °C, and (c) the post-annealed Co$_3$O$_4$ at 550 °C.

To confirm the composition of pre-annealed 450 °C and 550 °C samples, X-ray photoelectron spectroscopy (XPS) analysis was performed as displayed in Figure 2. The pre-annealed and the annealed 450 °C samples have similar full survey spectra. The Co 2p spectra for the pre-annealed appeared at the value of binding energy for 778 ± 0.5 and 800 ± 0.5 eV, whereas the annealed 450 °C appeared at the value of binding energy for 778 ± 0.5 and 793 ± 0.5 eV. The spectra of the pre-annealed are present in a broad area compared to the Co 2p spectra for the annealed 450 °C. The broad value of the pre-annealed perhaps is caused by water or solvent contaminant. A similar trend was also reported by Chen et al. (2020) on the annealing effect on MoS$_2$ [29]. The 2p$_{3/2}$ and 2p$_{1/2}$ peaks separation for both pre-annealed and annealed 450 °C samples are around ± 10 eV. According to H. Jadhav et al., between the 2p$_{3/2}$ and 2p$_{1/2}$ peaks, an energy difference of ~15 eV is characteristic of the Co$_3$O$_4$ phase [30]. The major peak in Co 2p$_{3/2}$ for the sample annealed at 450 °C de-convoluted into two peaks centered at 776.96 and 778.90 eV, which corresponded to Co$^{3+}$ and Co$^{2+}$ species, respectively. For the Co 2p spectrum of the 550 °C thin film, the Co$^{3+}$ and Co$^{2+}$ species were located at 777.07 and 778.95 eV, respectively. In addition, the presence of CoO was confirmed by the indication of a low appearance of satellites [31]. The Co 2p spectrum of single-phase Co$_3$O$_4$ showed a clear image of weaker peaks compared with that associated with CoO in the mixed phase of Co$_3$O$_4$/CoO [32]. Figure 2c shows the O 1s XPS spectra of the pre-annealed, annealed 450 °C, and annealed 550 °C samples. All samples produce oxygen peaks in different binding energy and height. The oxygen peaks of pre-anneal sample present at 529 and 530.6 eV. Meanwhile, the position oxygen peaks of annealed 450 °C and 550 °C samples are in lower binding energy, that is, at 527 and 528.6 eV. They differed only in the slight shifting in intensity and the peak position, thereby indicating that some oxygen atoms bind with different oxidation states of Co.
3.2. Structure and Morphology Characterization

The structure and morphology of the formed thin films were tested and confirmed by FESEM analysis. Figure 3 shows the morphology of the photoelectrode prepared at different annealing temperatures, namely, (a) pre-annealing, (b) 450 °C, and (c) 550 °C. The pre-annealed photoelectrode surface formed a uniformly grown flower-like structure. The high magnification FESEM images in Figure 3a revealed the formation of microscale flowers, which are composed of micro-sized petals with an average thickness of ~6 µm. According to Zhu et al., urchin-like spheres are composed of Co$_3$O$_4$. When the annealing temperature increased to 450 °C, the color of the photoelectrode changed from purple to black. FESEM observation revealed that the Co$_3$O$_4$ produced a microflower that started to decompose (Figure 3b). With increasing annealing temperature, the Co$_3$O$_4$ changed to mixed phase Co$_3$O$_4$$\cdot$CoO, and the morphology of the sample changed to microflowers with less thick nanowire petals (Figure 3c) [33].
Figure 3. FESEM images of (a1–a3) pre-annealed sample, (b1–b3) 450 °C sample, and (c1–c3) 550 °C sample.

Details of the microstructures of Co$_3$O$_4$ and mixed Co$_3$O$_4$·CoO were examined using HRTEM, and specifics were examined with selected area electron diffraction (SAED) (Figure 4). Lattice fringes of Co$_3$O$_4$ annealed at 450 °C are shown in Figure 4(a1–a3). The SAED of Co$_3$O$_4$ shown in Figure 4(a3) reveals the ring and spot pattern in a well-defined manner, demonstrating that the Co$_3$O$_4$ sample was highly crystalline. However, for the mixed Co$_3$O$_4$·CoO annealed at 550 °C, the SAED showed a small spot that made rings, which were designated as polycrystalline. According to Andrews et al., (1971) each spot arising from brag was reflected from individual crystalline [34]. As shown in Figure 4(b3), a SAED ring demonstrated the presence of a mixed phase that was well-blended at this phase. The first ring indicated Co$_3$O$_4$, whereas the second ring indicated CoO.

3.3. Optical Measurements

The optical properties of the photoelectrode samples were analyzed using a UV-Vis-NIR spectrophotometer. The optical absorption of the prepared photoelectrode samples and their corresponding Kubelka–Munk plots are shown in Figure 5, in which the pre-annealed samples showed an absorption region at 400–600 nm. Accordingly, the corresponding K-M plots exhibited a band gap value of 4.30 eV (Figure 5b). The pre-annealed sample exhibited absorption at much lower wavelengths and a large band gap, because the pre-annealed sample was not activated. For the sample prepared at 450 °C, the intensity of the light absorption was greater than that of the pre-annealed sample, which covered a wider range of the light spectrum, ranging from 200 to 900 nm (Figure 5a). Within this light spectrum range, two main broad peaks were identified, between 200–500 and 580–900 nm. Correspondingly, two main broad peaks were identified with two band gaps of 2.00 and 2.50 eV (Figure 5b). This observation suggested that a higher temperature was required to affect the phase transformation of the pre-annealed sample. This suggestion was supported by the XRD analysis result, in which an identical phase of Co$_3$O$_4$, as identified in the
pre-annealed sample, was also detected in the sample prepared at 450 °C. However, after annealing, the band gap values significantly shifted to smaller values. This shifting pattern of the band gap value could be an indication of the intermediate phase transformation. In general, Co₃O₄ is known as “Co₂O₃/CoO,” which represents two constituents in the material. Therefore, these constituents might contribute to the creation of two optical absorption peaks. The first band (500–700 nm) can be referred to as the O²⁻ → Co²⁺ charge transfer process of CoO, whereas the second absorption band (250–500 nm) can be attributed to the O²⁻ → Co²⁺ charge transfer of Co₂O₃ [35,36].

![HRTEM images](image1.png)

**Figure 4.** HRTEM images of (a1–a3) 450 °C and (b1–b3) 550 °C samples inserted with SAED and lattice fringes.

![UV-Vis absorption](image2.png)

**Figure 5.** (a) UV-Vis absorption, and (b) curves band gap determination by Kubelka-Munk plot of samples pre-annealed and annealed at 450 °C and 550 °C.

As the annealing temperature was increased to 550 °C, the intensity of absorption significantly decreased; only one absorption peak that signaled between 200 and 450 nm remained. Extrapolation of K-M plots on the x-axis found that the band gap value was narrowed to a single band gap value of 3.1 eV (Figure 5b). When the as-prepared Co₃O₄ was annealed with a nitrogen gas flow, and the temperature was increased, Co²⁺ was protected against oxidation, thereby ensuring the production of CoO nanowire. Oxygen vacancies occurred during annealing in an oxygen-deficient atmosphere, and this formation
was associated with the energy band gap. A narrowing of the band gap was the result of the increase in oxygen vacancies, and hence, the increase in the visible light absorption.

3.4. Photoelectrochemical Testing

3.4.1. The Effect of the Type of Electrolyte on the Photocurrent Generation

The photoelectrochemical activity of the samples was measured based on different types of electrolytes that represented different pH values, namely, 0.5 M Na₂SO₄ (pH 6.7), 0.5 M KOH (pH 13), and 0.5 M H₂SO₄ (pH 1) (Figure 6). Based on the linear sweep voltammetry data, both photocathode samples exhibited similar patterns of photocurrent generation with similar photocurrent density values in all types of electrolytes. Based on Figure 6a–c among the electrolytes under investigation, the photocurrent generation measured in H₂SO₄ solution was the highest. Photocurrent produced by the pre-annealed sample is ~−0.023 mA cm⁻². This photocurrent value was approximately four-fold greater than that achieved in neutral and basic electrolytes. Meanwhile, the highest photocurrent produced by sample 450 °C (~−2.3 mA cm⁻² at −0.5 V vs. RHE) was much higher than the Co₃O₄ pre-annealed sample. According to Zhao et al. (2012) increasing annealing temperature may improve catalytic activity because high temperature may increase the structural defects and the number of active sites, which would have positive impacts on the catalytic activity. However, at sample 550 °C, the photocurrent decreased to ~−1.2 mA cm⁻² at −0.5 V vs. RHE because the phase of the sample has changes. These results suggest that H₂SO₄ electrolyte solution enriched with protons (H⁺) could sufficiently attract oppositely charged electrons. The present study suggested that the recombination rates of electrons and holes were remarkably reduced, leading to enhanced photocurrent generation. Furthermore, a chronocamperometry stability test was conducted for samples of 450 °C and 550 °C in 0.5 M H₂SO₄ electrolyte (Figure 6c). Sample 450 °C shows better stability compared to sample 550 °C. Under constant simulated solar illumination and fixed current density of 0.4 mA cm⁻², the 450 °C sample was stable until 4000 s of irradiation time before slowly decreasing. Meanwhile, the 550 °C sample was only stable for less than 500 s and decreased drastically.

3.4.2. Electrochemical Impedance Studies

Electrochemical impedance analyses (EIS) of the as-prepared samples were conducted to qualitatively examine the charge transfer resistance (Rct) through Nyquist plotting, as shown in Figure 7a. The pre-annealed sample had high resistance compared to the annealed samples at 450 °C and 550 °C. The Rct was evaluated based on the size of the semicircle, wherein the smallest size of the semicircle represented the lowest Rct. The effect of electrolyte on the Rct was further conducted to the annealed 450 °C sample, where the smallest semicircle was produced when EIS testing was conducted in H₂SO₄ solution. Correspondingly, the extent of Rct evaluated herein explained the results obtained in the measurement of photocurrent generation, as shown in Figure 6. In this case, the lowest Rct improved the efficiency of charge transfer from the semiconductor to the electrolyte and vice versa, consequently yielding the highest photocurrent.
The chronopotentiometric stability of annealed 450 °C and 550 °C samples in H2SO4 electrolyte.

The charge carrier was analyzed from the flat band, wherein flat band is activity. However, at sample 550 °C, the photocurrent decreased to ~0.023 mA cm².

Mott-Schottky (M-S) Plot implementation of M-S analysis on annealed samples of 450 °C and 550 °C was performed for (a) 450 °C in different electrolytes, (b) the evaluation of different samples prepared at 450 °C and 550 °C using different electrolytes, and (d) The chronopotentiometric stability of annealed 450 °C and 550 °C samples in H2SO4 electrolyte.

Figure 6. Photocurrent density curve for samples annealed at (a) Pre-annealed, (b) 450 °C, (c) 550 °C using different electrolytes, and (d) The chronopotentiometric stability of annealed 450 °C and 550 °C samples in H2SO4 electrolyte.

Figure 7. The derivation of charge transfer resistance (Rct) from Nyquist plot through EIS analysis for (a) 450 °C in different electrolytes, (b) the evaluation of different samples prepared at 450 °C and 550 °C using H2SO4 at pH 1, and (c,d) Mott–Schottky plots of the thin films annealed at 450 °C and 550 °C in 0.5 M H2SO4.
3.4.3. Mott-Schottky (M-S) Plot

M-S Analysis was done to study the charge carrier concentration of samples. The implementation of M-S analysis on annealed samples of 450 °C and 550 °C was performed in H₂SO₄ (pH 1). The charge carrier was analyzed from the flat band, wherein flat band is the potential at which the potential drop between the electrode surface and the bulk is zero. This can establish the position of semiconductor energy band with respect to the redox potential. The intrinsic value of flat band (V_{FB}) and carrier density (N_A) for both samples can be extracted from the x-intercept and slope of the plot between the reciprocal of the square 1/C² and the bias potential (Figure 7c), in accordance with the Mott–Schottky equation, as follows (Equation (1)) [37]

\[
\frac{1}{C^2} = \left(\frac{2}{\epsilon e \varepsilon_o N_A}\right) \left[V - V_{FB} - \frac{K_B T}{e}\right]
\]

where \(\epsilon\) is the electronic charge, \(\varepsilon\) is the relative permittivity of CoO (12.9), \(\varepsilon_o\) is the permittivity of vacuum, \(K_B\) is Boltzmann’s constant, and \(T\) is the absolute temperature [38]. A negative slope from all samples implied a p-type semiconductor. The extrapolation of slopes from the M-S plot (Figure 7) when integrated into the gradient of Equation (1) gives the \(N_A\). The interception of slopes at x-axis represents the \(V_{FB}\). In this case, the calculated value of \(N_A\) was 1.24 × 10¹¹ and 3.99 × 10¹⁶ for 450 °C and 550 °C samples.

However, the valence band (\(V_B\)) of the samples was determined using the following equation (Equation (2))

\[
E_{FB} - E_{VB} = k_B T \ln \frac{N_V}{N_A}
\]

where \(N_V\) is the effective density of states in the valence band (\(V_B\)). The \(N_V\) can be expressed as follows (Equation (3))

\[
N_V = 2 \left(\frac{2\pi m^* k_B T}{\hbar^2}\right)^{3/2}
\]

Incorporating the band gap energy (\(E_g\)) determined earlier (Figure 7), the conduction band (\(C_B\)) of the samples can be determined [39]. The analyzed data of \(V_{FB}, V_B, E_g,\) and \(C_B\) are arranged as depicted in Figure 8. For this purpose, the potential measurements in Ag/AgCl were converted to the RHE using the following equation (Equation (4))

\[
E_{RHE} = E_{Ag/AgCl} + E_{0}^{Ag/AgCl} + 0.059pH
\]

where \(E_{0}^{Ag/AgCl} = 0.197\) V at 25 °C.

To electrochemically split the water molecule, the band edges of the photoelectrode need to be in straddle position to the water molecule redox potential, which means the \(C_B\) of the material should lie at a more negative potential than the water reduction potential. Meanwhile, the \(V_B\) position should lie at a more positive potential to the water oxidation potential. Based on the calculation, the resultant band edges of \(C_B\) and \(V_B\) of both samples are as illustrated in Figure 8. The energy band structure of sample prepared at 450 °C (Co₃O₄) is shown in Figure 8; the \(C_B\) and \(V_B\) are −1.04 eV and 0.98 eV. The band edges in this study were found at the more negative potential of our previous study; the \(C_B\) and \(V_B\) of Co₃O₄ are estimated to be −0.55 and 1.10 eV, respectively [12]. Both the \(C_B\) and \(V_B\) located were at a more negative potential of H⁺ to H₂ and oxidation potential of H₂O to O₂, respectively [35]. A similar trend was also found in the sample prepared at 550 °C. Given that the bandgap of the sample prepared at 550 °C was bigger than the sample prepared at 450 °C, the \(C_B\) position falls at more negative potential than the 450 °C sample. Meanwhile, the \(V_B\) position is not much different. This result showed that both cobalt oxides resulting in this study do not straddle to the redox potential of water splitting, but it can be used to produce hydrogen only [40].
Figure 8. Band alignment of Cobalt Oxide thin film annealed at 450 °C and 550 °C against potential redox of water molecule.

4. Conclusions

This work provided the necessary support for the direct growth of cobalt oxide on FTO thin films, the effect of annealing on the phase transformation of cobalt oxide, and the effect of electrolyte on the PEC water-splitting application. The annealing temperature affected the phase of cobalt oxide thin films and changed the morphology from microflower Co$_3$O$_4$ to urchin-like Co$_3$O$_4$/CoO mixed phase. A single phase of CoO could not be produced by direct growth on FTO through the hydrothermal method due to the sensitivity of FTO to temperatures higher than 550 °C. In addition, the electrolyte affected the performance of PEC water splitting. H$_2$SO$_4$ resulted in a higher photocurrent density than Na$_2$SO$_4$ and KOH. According to the measured photocurrent generation, the highest value was contributed by the single-phase sample of Co$_3$O$_4$ from the annealed at 450 °C. The stability test also showed that the Co$_3$O$_4$ from the annealed at 450 °C is more stable than the mixed-phase produced by the annealed at 550 °C. This study found that the bandgap and band edges of the cobalt oxide thin films produced from the direct hydrothermal method slightly different from the powder results, in which powder cobalt oxide produces a more appropriate band structure to the PEC water-splitting application.

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