Thickness-dependent photoelectrochemical properties of a semitransparent Co₃O₄ photocathode

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Abstract
Co₃O₄ has been widely studied as a catalyst when coupled with a photoactive material during hydrogen production using water splitting. Here, we demonstrate a photoactive spinel Co₃O₄ electrode grown by the Kirkendall diffusion thermal oxidation of Co nanoparticles. The thickness-dependent structural, physical, optical, and electrical properties of Co₃O₄ samples are comprehensively studied. Our analysis shows that two bandgaps of 1.5 eV and 2.1 eV coexist with p-type conductivity in porous and semitransparent Co₃O₄ samples, which exhibit light-induced photocurrent in photoelectrochemical cells (PEC) containing the alkaline electrolyte. The thickness-dependent properties of Co₃O₄ related to its use as a working electrode in PEC cells are extensively studied and show potential for the application in water oxidation and reduction processes. To demonstrate the stability, an alkaline cell was composed for the water splitting system by using two Co₃O₄ photoelectrodes. The oxygen gas generation rate was obtained to be 7.17 mL·h⁻¹·cm⁻². Meanwhile, hydrogen gas generation rate was almost twice of 14.35 mL·h⁻¹·cm⁻² indicating the stoichiometric ratio of 1:2. We propose that a semitransparent Co₃O₄ photoactive electrode is a prospective candidate for use in PEC cells via heterojunctions for hydrogen generation.

Introduction
Hydrogen production using water splitting in photoelectrochemical (PEC) cells may help to overcome challenges in the conversion and storage of solar energy. Most of the metal oxides are earth-abundant, non-toxic, stable and easy to synthesise, and hence attractive regarding low-cost and reliable PEC cells [1-8]. For a widespread application of PEC cells, the photoelectrodes need to fulfill the criteria of (i) a low band gap (1.7–2.2 eV), (ii) low resistivity, (iii) low cost, (iv) corrosion stability and (v) a correct alignment of band edges with respect to the water redox potential [3,9,10]. The spinel Co₃O₄ is interesting...
because of its dual bandgap (1.5 and 2.2 eV), high absorption coefficient, intrinsic p-type doping and chemical stability. It has found application as a light-absorbing entity in all-metal-oxide photovoltaic cells [11-17]. Dual-bandgap CoO4 films provide distinct band states in the energy–momentum diagram, which is advantageous to reduce the thermalisation-related losses in the sunlight-driven hydrogen generation. Dual bandgaps in CoO4 originate from the crystal-field split Co 3d states at the octahedral (Co3+) and tetrahedral (Co2+) cobalt sites, where Co vacancies are the dominant sources of the p-type conductivity of CoO4 under oxygen-rich conditions [9,13]. Despite these interesting properties of CoO4 its application in photocathodes has been rarely studied [18-23]. Existing studies have measured a photocurrent of 33.6 μA·cm⁻² in 0.5 M Na₂S on a mesoporous CoO4 nanosheet grown through in situ transformation from hexagonal Co(OH)₂ to spinel CoO₄ [18]. Hong et al. demonstrated a photocurrent of 0.4 mA·cm⁻² from CoO4 nanowire photocathodes, which could be enhanced to 4.5 mA·cm⁻² with Ag nanowires [24]. Interestingly, a high photocurrent density of 29 mA·cm⁻² can be achieved from CoO4 under one-sun illumination (AM1.5G) suggesting a high (solar-to-hydrogen) efficiency of 35.8% [3].

Studies using CoO4 as a catalyst have explored the oxygen evolution reaction (OER) [25,26] and the hydrogen evolution reaction (HER) [20,27] to prove its outstanding stability [28] for the use in water-splitting applications. It therefore may be applied as a protective heterojunction layer to overcome the typical overpotential in photoactive materials. Examples of materials used in such applications include Cu₃O [19,29], CdS [30], TiO₂ [31], Fe₂O₃ [32], and BiVO₄ [33,34]. To absorb light with CoO₄, an adequately thick film is required. However, the low mobility of photogenerated charge carriers in CoO₄ can result in a low carrier lifetime, which is detrimental for efficient charge collection in photoactive applications [9,13,20]. In this context, relatively thin Co₃O₄ samples can overcome charge collection problems due to its semitransparency, which has been investigated in this study. To fabricate Co₃O₄ samples, Kirkendall diffusion is effective to induce the thermal oxidation of Co under atmospheric conditions, which provides an enhanced surface area due to porous features [19,32-38].

Our previous study on porous Co₃O₄ films grown by Kirkendall diffusion exhibited efficient photoelectrocatalystical seawater splitting due to its favourable HER properties [20]. We also developed compact Co₃O₄ films by a reactive sputtering method, in which sputtered Co particles were converted into a compact Co₃O₄ film by controlling the flowing O₂ gas, to offer a self-powered ultraviolet photodetector [17] and semitransparent photovoltaics [39]. It is noteworthy to mention that Co₃O₄ films grown by Kirkendall diffusion have the advantages of a porous structure, a higher growth rate, and easy fabrication.

Here, we report thickness-controlled Co₃O₄ photoactive electrodes in PEC cells that include the water oxidation and the reduction potentials. We thermally oxidize Co nanoparticles in air that form a porous semitransparent Co₃O₄ layer through Kirkendall diffusion. The structural, physical, optical, electrical and photoelectrochemical properties of Co₃O₄ samples are presented as functions of the thickness. The alkaline cell was composed for water splitting by using two Co₃O₄ photoelectrodes. We propose a promising route for photoactive, semitransparent Co₃O₄ embedded in PEC cells for the light-driven hydrogen generation through water splitting.

Results and Discussion

The oxidation of Co nanoparticles formed a porous Co₃O₄ structure due to the nanoscale Kirkendall effect as shown in Figure 1a, which arises from the difference in diffusion rates between the anions and cations [35,40]. We applied rapid thermal oxidation to sputtered Co nanoparticles in air at 500 °C for 10 min to convert them into CoO₄ [20]. Co films of varying thickness were deposited using large-area (4 inch diameter) sputtering on glass and FTO/glass substrates. Identical rapid thermal processing (RTP) oxidation was applied to these Co films to allow the formation of Co₃O₄ films of varying thickness and porosity.

Figure 1b shows the XRD pattern of two prepared Co₃O₄ samples, 70 nm and 230 nm thick, grown on the FTO/glass substrate. XRD confirmed the formation of a crystalline Co₃O₄ phase due to the air-induced diffusion-driven oxidation of Co. XRD peaks corresponding to Co₃O₄ and F:SnO₂ (substrate) were identified and marked. A stronger XRD peak at 2θ = 36.81° corresponds to the (311) planes of cubic Co₃O₄ with a d-spacing of 2.41 Å, in agreement with the crystallographic open database file COD-9005888. According to this XRD pattern, the Co₃O₄ material has a lattice parameter of a = 8.09 Å (cubic, a = b = c). The XRD peaks at 18.90°, 31.20°, 44.73°, 59.30°, and 65.12° correspond to the (111), (220), (400), (511), and (404) crystal planes, respectively [20,41].

When compared to the F:SnO₂ substrate material, the XRD peaks corresponding to the 230 nm thick Co₃O₄ sample are more intense. The absence of XRD peaks of pure Co indicates that the applied RTP fully oxidized the Co film into a Co₃O₄ film with controlled thickness and porosity, which is further validated below.

Figure 1c,d shows the surface morphology of both the deposited Co and the RTP-grown Co₃O₄ film on the glass substrate, re-
respectively. FESEM results confirm that the deposited film contains spherical Co particles, and conversion into porous Co$_3$O$_4$ is attributed to Kirkendall-diffusion-induced thermal oxidation.

The planar morphology is shown in Figure 1e and Figure 1f, and corresponds to 70 nm and 230 nm thick Co$_3$O$_4$ films grown on the FTO substrate, respectively. The as-grown Co$_3$O$_4$ films are uniform and interconnected. A cross-sectional FESEM image of the 70 nm thick Co$_3$O$_4$ film, shown in Figure 1g, reveals compact and dense features, while the 230 nm thick Co$_3$O$_4$ film, seen in Figure 1h, reveals porous features uniformly distributed across the FTO surface. This subtle morphology change in the crystalline Co$_3$O$_4$ can be applied to grade its porosity by simply varying the Co thicknesses prior to thermal oxidation. Therefore, we prepared Co$_3$O$_4$ samples with varying thicknesses from 70 to 230 nm, which were extensively studied with regard to their optical, electrical, interfacial, and photoelectrochemical cell properties.

Figure 2a shows the thickness-dependent transmittance ($T$) and absorbance ($A$) spectra of the Co$_3$O$_4$ samples. Interestingly, all the Co$_3$O$_4$ samples exhibited fair absorbance with semitransparent optical properties. Absorbance dominates the shorter wavelengths ($\lambda = 300–500$ nm) with transmittance dominating at longer wavelengths from 600 nm to the infrared (IR). Two distinct transitions in both the $T$ and $A$ spectra of all Co$_3$O$_4$ samples are attributed to two bandgaps coexisting in the Co$_3$O$_4$ material. A 70 nm thick Co$_3$O$_4$ sample exhibited a higher $T$ in the IR region than the other Co$_3$O$_4$ samples, which is attributed to its dense and compact film, which causes lower absorption of free carriers than the porous surface.

The absorption coefficient ($\alpha$), which determines the absorption length of the Co$_3$O$_4$ samples was estimated using the relation

$$\alpha(\lambda) = \frac{1}{d} \ln \left( \frac{(1-R(\lambda))^2}{T(\lambda)} \right),$$
where $d$ and $R$ are the thickness of the Co$_3$O$_4$ layer and the reflectance, respectively. Figure 2b shows $\alpha$ estimated as a function of photon energy ($\hbar\nu$). The influence of the Co$_3$O$_4$ morphology on $\alpha$ is interesting. Except for the 70 nm film, $\alpha$ increases with thickness, suggesting an increase in porosity as well. A higher porosity led to higher $\alpha$ values, which are prominent in the 440–350 nm region. This feature is useful for a porous Co$_3$O$_4$ material as a semitransparent electrode in water-splitting PEC cells. Moreover, two distinct transitions (positive slope) around 1.5 and 2.4 eV in Figure 2b have different $\alpha$ values, providing optical selectivity that can be controlled by film thickness.

Having identified this useful semitransparency of Co$_3$O$_4$, we prepared working electrodes to study the thickness-dependent performance of the photoelectrochemical cell. Figure 2c shows a semitransparent Co$_3$O$_4$ working electrode with an active area of 1 cm$^2$. Clear epoxy resin was applied to the rest of the surface to prevent an electrical connection to the working terminal of the potentiostat/galvanostat. Co$_3$O$_4$ has evolved as a chemically resistive and stable material for electrolysis reactions [20,25-27], and therefore the potential of the Co$_3$O$_4$ working electrode was swept from 1.5 to $-0.3$ V vs RHE in a 0.1 M NaOH electrolyte (pH 12.5). The thickness-dependent linear sweep voltammogram (LSV) of the PEC cell under chopped light illumination is shown in Figure 2d. These results provide an overview of the photoinduced OER at 1.23 V vs RHE, the HER at 0 V vs RHE, and the operation of the photocathode. The value of the onset potential ($V_{on}$), which is the condition attributed to a minimum charge transfer of the cell, was found to be...
just below that of the OER potential. All of the Co$_3$O$_4$ samples exhibited a photoresponse, suggesting photoabsorption and the utilization of photogenerated charges in the PEC cells. A strong thickness dependence on the photoresponse was found and showed that thicknesses of 100–170 nm are adequate to gain significant photocurrents. More interestingly, the 170 nm Co$_3$O$_4$ sample exhibited maximum photocurrent values in the applied potential region of 0.2–0.4 V vs RHE as described below in detail. It is fundamental to optimise the thickness of the Co$_3$O$_4$ film. In order to improve light absorption, a thicker film is better. However, the Co$_3$O$_4$ film has a short carrier diffusion length due to the slow electron extraction kinetics, resulting in a degraded conversion efficiency [14]. This is the reason for the current decrease for the relatively thick Co$_3$O$_4$ films from 170 to 230 nm.

The thickness-dependent LSV for the potentials applied to the Co$_3$O$_4$ photoelectrode includes the water oxidation and reduction potentials as shown in Figure 3a–c. The photoresponse of the Co$_3$O$_4$ samples in the potential range from –0.25 to 0.2 V vs RHE corresponds to the hydrogen evaluation reaction as shown in Figure 3a. The Co$_3$O$_4$ samples with thicknesses from 100 to 230 nm showed identical photocurrent values of ca. 1 mA·cm$^{-2}$. An increased dark-current level, indicating catalytic properties of the Co$_3$O$_4$ material, may have an advantage as the photoinduced current is of great interest in achieving photoinduced water reduction reactions in PEC cells.

When the PEC cell containing the Co$_3$O$_4$ working electrode went to the depletion region from a flat band condition, the photoresponse was prominent, as shown in Figure 3b. The low dark current ($J_0$), which is consistent throughout the potential from 0.8 to 0.1 V vs RHE, confirms the chemical stability of the Co$_3$O$_4$ material. Meanwhile, these results also characterized the photoactive properties of the depletion region and its modulation in the Co$_3$O$_4$ electrode. The height of the spikes seems to be related to the bias voltage.

Figure 3c shows the LSV photoresponse near the onset potential of 1.05 V vs RHE, the $V_{on}$ region, for all the samples confirming that the variation in thickness and porosity do not affect $V_{on}$. However, thicker samples exhibited a higher photocurrent density in the anodic region, which can be interesting for studying the possibilities of light-induced water oxidation reactions. In this context, specifically, the Co$_3$O$_4$ film with a thickness of 200 nm showed a photocurrent density ($J_{photo}$) up to 120 µA·cm$^{-2}$ at 1.23 V vs RHE.

For precise observation, we provided the morphologies of the 170 nm thick Co$_3$O$_4$ film in Figure 4. The FESEM images clearly showed the pores (diameter 14–20 nm) and the nanocrystals (diameter 24–42 nm). Through the pores the surface area of Co$_3$O$_4$ film can be enhanced. Meanwhile, the nanocrystals work as the efficient routes for charge collection.

Next, the current–time characteristics of the 170 nm thick semitransparent Co$_3$O$_4$ photocathode were studied in transient light as shown in Figure S1 (Supporting Information File 1). Chronoamperometry studies at 0 V vs RHE for the Co$_3$O$_4$ photocathode show an initial $J_{photo} = 0.7$ mA·cm$^{-2}$ that stabilized to 0.55 mA·cm$^{-2}$ after 30 min of operation, demonstrating a stable PEC cell operation. This also indicates that porous

![Figure 3](image-url)
Co$_3$O$_4$ can be a candidate for a semitransparent photocathode as a chemically stable and optically active material.

In order to better understand the photoactivity and semitransparency of the Co$_3$O$_4$ photocathode, transmission electron microscopy was performed on the 170 nm thick Co$_3$O$_4$ sample as shown in Figure 5a–c. The cross-sectional TEM image of the Co$_3$O$_4$ photocathode seen in Figure 5a shows the flawless Co$_3$O$_4$/FTO interface, which is desirable for efficient transport of photogenerated charges. Moreover, the TEM image shows the nanocrystalline nature of the porous Co$_3$O$_4$ due to the Kirkendall diffusion that drove the thermal oxidation of Co nanoparticles on the FTO layer. The bright-field distribution observed from the TEM image further illuminates the porous features of the Co$_3$O$_4$ nanocrystals and the enhanced photocurrent in the PEC cell performance.

Figure 4: Surface morphology of the 170 nm thick Co$_3$O$_4$ film on FTO/glass showing (a) the pores with diameters of 14–20 nm and (b) Co$_3$O$_4$ nanocrystals with diameters of 24–42 nm.

Figure 5: (a) Transmittance electron micrograph featuring nanocrystalline features of a Co$_3$O$_4$ electrode prepared on FTO/glass. (b) Cross-sectional image and (c) elemental line profile of Co$_3$O$_4$/FTO/glass electrode. (d) Tauc’s relation showing the values of two direct bandgaps in Co$_3$O$_4$ and their dependence on the thickness of the film. (e) Thickness-dependent Mott–Schottky characteristics of Co$_3$O$_4$/FTO electrodes.
A complete cross-sectional image of the Co$_3$O$_4$/FTO/glass using the TEM is shown in Figure 5b. This confirms a void-free interface, which is typically difficult to obtain in samples grown using Kirkendall diffusion oxidation, as it generally leads to a core–shell structures. However, here it yielded a porous Co$_3$O$_4$ film that can be applied in water-splitting devices. An elemental line profile garnered from energy dispersive spectroscopy as shown in Figure 5c supports the claim of porosity in the grown Co$_3$O$_4$ film and the void-free interface between Co$_3$O$_4$/FTO.

Further, we estimated the thickness-dependent band-gap energies ($E_g$) of the Co$_3$O$_4$ samples using Tauc’s relation as shown in Figure 5d. The coexistence of bandgaps two distinct band gaps with direct $E_g$ values of around 1.5 and 2.1 eV is confirmed. Due to the porous and nanocrystalline nature of the Co$_3$O$_4$ samples, a blueshift in the $E_g$ values is seen, compared to the dense 70 nm thick Co$_3$O$_4$ sample. Table 1 shows the summarized thickness-dependent optical and electrical properties of the Co$_3$O$_4$ samples.

Mott–Schottky (MS) characteristics allow us to describe the type of conductivity, free carrier concentration, and flat-band potential ($V_{FB}$) of the samples. Figure 5e shows the thickness-dependent MS characteristics ($1/C^2$) as a function of $V$ vs RHE) of the Co$_3$O$_4$ samples, obtained at an applied frequency of 5 kHz and under dark conditions. The negative slope in the MS characteristics indicates a p-type material, and the two distinct slopes correspond to two $E_g$ values. The intersect of the $1/C^2$ values on the potential axis indicates the flat-band potential, for which band edges are flat and PEC cells under this condition exhibit the minimum charge transfer. Additional details on the identification of band edges and $V_{FB}$ in the Co$_3$O$_4$ samples can be found elsewhere [20]. Figure S2 and Figure S3 (Supporting Information File 1) provide analysis of the MS characteristics including the values of $N_{A1}$, $N_{A2}$, $V_{FB1}$, and $V_{FB2}$, which are also summarized in Table 1, where $N_A$ is the acceptor carrier concentration. Thickness-dependent parameters including the $T$, $E_g$, and $N_A$ values of the Co$_3$O$_4$ samples suggest that the enhanced photocurrent performance of the PEC cell containing a 170 nm thick Co$_3$O$_4$ film are primarily due to its enhanced porosity and optical absorption. We also studied the thickness dependent optical and electrical properties of Co$_3$O$_4$ film grown by reactive sputtering [17]. In fact, we can see the systematic variation of Mott–Schottky characteristics, and so of the $V_{FB}$ and $N_A$ values of the samples grown by Kirkendall diffusion. This variation is attributed to the varying porosity that does not occur shown in the compact Co$_3$O$_4$ film [20].

In order to investigate the long-term stability, the PEC cell was tested for 24 h as shown in Figure 6a. The PEC cell has dual Co$_3$O$_4$ electrodes with a potential of 1.65 V vs a Co$_3$O$_4$ electrode in 400 mL of an alkaline bath (1 M KOH). The measured current value is presented in Figure 6b for a current density of 25 mA·cm$^{-2}$ that is stable over a period of 24 h. In order to see the morphological changes after 24 h, the Co$_3$O$_4$ electrodes were observed by using FESEM as shown in Figure 6c. The OER side of the Co$_3$O$_4$ film seems to be similar to a pristine film. The HER side of the Co$_3$O$_4$ electrode is also in good shape. As a reference, the FTO image is also presented.

Further, varying bias values (1.4, 1.7 and 2 V) were applied to monitor the water-splitting reaction. Figure 6d shows bias-dependent current profiles. At 1.4 V a current density of 5.25 mA·cm$^{-2}$ with a photocurrent density of 0.75 mA·cm$^{-2}$ under illumination was observed. With an enhanced bias of 2 V, a significantly enhanced photocurrent density (6.5 mA·cm$^{-2}$) was obtained. This result clearly shows the potential of the Co$_3$O$_4$ electrode to achieve high photocurrents at a relatively low potential value. The obtained photocurrent density value for overall water splitting from dual Co$_3$O$_4$ electrodes in alkaline bath is more efficient in terms of the required overpotential than the seawater splitting (Co$_3$O$_4$|Pt electrodes) in our previous report [20].

In order to verify the PEC performance, a PEC cell with dual Co$_3$O$_4$ electrodes was set up for volumetric measurements. The Co$_3$O$_4$ electrodes were loaded into two separated vials (15 mL, Figure 7) and placed into the 1 M KOH electrolyte bath as shown in Figure 8a. A potential of 1.75 V was supplied (15 mL, Figure 7) and placed into the 1 M KOH electrolyte bath.

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**Table 1: Summarized properties of the Co$_3$O$_4$/FTO samples.** Here $t$, $T$, $\lambda$, $E_g$, $V_{FB}$ and $N_A$ are the thickness of the Co$_3$O$_4$ layer, transmittance, photon wavelength, band gap, flat-band potential, and acceptor carrier concentration, respectively.

<table>
<thead>
<tr>
<th>$t$ (nm)</th>
<th>$T$ (%)</th>
<th>$\lambda = 820$ nm</th>
<th>$E_g1$ (eV)</th>
<th>$E_g2$ (eV)</th>
<th>$V_{FB1}$ (V vs RHE)</th>
<th>$V_{FB2}$ (V vs RHE)</th>
<th>$N_{A1}$ (cm$^{-3}$)</th>
<th>$N_{A2}$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>53</td>
<td>39</td>
<td>1.45</td>
<td>2</td>
<td>0.7</td>
<td>0.18</td>
<td>4.9 × 10$^{20}$</td>
<td>6.1 × 10$^{19}$</td>
</tr>
<tr>
<td>100</td>
<td>41</td>
<td>24</td>
<td>1.47</td>
<td>2.16</td>
<td>0.84</td>
<td>0.32</td>
<td>2.5 × 10$^{20}$</td>
<td>9.7 × 10$^{19}$</td>
</tr>
<tr>
<td>170</td>
<td>35</td>
<td>15</td>
<td>1.49</td>
<td>2.14</td>
<td>0.82</td>
<td>0.06</td>
<td>8.8 × 10$^{19}$</td>
<td>5.0 × 10$^{19}$</td>
</tr>
<tr>
<td>200</td>
<td>29</td>
<td>8</td>
<td>1.5</td>
<td>2.13</td>
<td>0.93</td>
<td>0.3</td>
<td>1.4 × 10$^{20}$</td>
<td>5.3 × 10$^{19}$</td>
</tr>
<tr>
<td>230</td>
<td>25</td>
<td>4</td>
<td>1.51</td>
<td>2.12</td>
<td>0.7</td>
<td>0.08</td>
<td>2.5 × 10$^{20}$</td>
<td>1.1 × 10$^{20}$</td>
</tr>
</tbody>
</table>

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Evolution of the gases was clearly monitored in the two vials as presented in Figure 8b. After 23 min, 5.5 mL of hydrogen and 2.75 mL of were accumulated, corresponding to the ratio of 2:1 of water splitting. The hydrogen and oxygen gas evolution as a function of the time is presented in Figure 8c. The results show a hydrogen gas generation rate of 14.35 mL·h⁻¹·cm⁻² and an oxygen generation rate of 7.17 mL·h⁻¹·cm⁻² at a bias of 1.75 V vs Co₃O₄ electrode.

Our results demonstrate a stable photoinduced PEC cell performance with a semitransparent Co₃O₄ material made through an easy fabrication process. This could be of great interest for improving the water-splitting performance of emerging, earth-abundant light-absorber materials such as metal sulfides and metal oxides via heterojunction. The photocurrent can be further improved by three approaches: The first one is to improve the optoelectronic processes in the Co₃O₄ film [39], the second is to improve the composition of the heterojunction, i.e. Co₃O₄/Ga₂O₃ [42,43], and the third is the combination with a catalyst such as NiMo and transition-metal dichalcogenide 2D materials [43,44].

Conclusion

We fabricated porous, semitransparent Co₃O₄ working electrodes of varying thickness using Kirkendall diffusion thermal oxidation in air. The thickness-dependent structural, physical, optical and electrical properties of the porous Co₃O₄ samples
Figure 8: (a) Current density as a function of the time. The Co$_3$O$_4$ electrode was biased at 1.75 V in 1 M KOH electrolyte. Inset shows the photograph of gas evolution by time. (b) Photographs of the gas evolution at $t=0$ and $t=23$ min. (c) The hydrogen and oxygen gas evolution as a function of the time.

Experimental

Sample fabrication: The photocathode was composed of Co$_3$O$_4$/fluorine-doped tin oxide (FTO)/glass. The general synthesis of Kirkendall diffusion grown Co$_3$O$_4$ film was analogue to our previous study [20]. In brief, a commercial fluorine-doped tin oxide (FTO)-coated glass (735167, Sigma-Aldrich, sheet resistance of 7 $\Omega$/sq) and a glass microscope slide were used as substrates. These were cleaned using a sequence of isopropyl alcohol, acetone and distilled water using ultrasonication. Then, various thicknesses of Co films were deposited using a dc magnetron sputtering system (dc power ca. 10 W·cm$^{-2}$) was applied to a 4” Co target (purity 99.99%). At a base pressure of $5 \times 10^{-5}$ Torr sputtering gas (Ar) at a flow rate of 50 sccm was injected. To form the Co$_3$O$_4$ film, an atmospheric rapid thermal processing was applied at 550 °C for 10 min. The processing temperature was achieved in two stages. Ramp 1 increased the room temperature of 25 to 300 °C in 5 min. Ramp 2 then increased the temperature from 300 to 550 °C in 5 min. Natural cooling followed the RTP and at 100 °C samples were removed from the RTP chamber for characterization and electrochemical studies.

The Co$_3$O$_4$ working electrode was made of Teflon-coated wire that was applied to the FTO film with Kapton tape. Then, a clear insulating epoxy was applied to the Kapton tape and glass edges to provide a working area of 1 cm$^2$.

Materials characterization: In order to examine the crystalline structure of Co$_3$O$_4$, an X-ray diffraction microscope (XRD, Rigaku, SmartLab) (Cu Kα radiation, $\lambda = 1.540598$ Å, in grazing mode with a glancing angle of 0.5°, step size of 0.05°, and a 20 range of 10–80°) as well as a field-emission transmission electron microscope (FETEM, JEOL, JEM-2100F) were used. Cross-sectional TEM samples were prepared using a focused ion beam system (FIB, FEI, Quanta 3D FEG).
elemental compositions in the cross sections of the Co$_3$O$_4$ layers in the working electrode were determined as line profiles by an energy dispersive spectroscopy (EDS) attachment to the FESEM. Thickness and average surface roughness of the deposited films were characterized using a surface profiler (Vecco, Dektak XT-E). The planar and cross-sectional morphologies were analysed using a field-emission scanning electron microscope (FESEM, JOEL, JSM_7800F) with 5 kV of field voltage, using an SE2 secondary detector. Optical characterization was carried out using a UV–visible spectrophotometer (Shimadzu, UV-2600) by recording the transmittance, absorbance, and reflection of the Co$_3$O$_4$ films in the range of 300–1100 nm.

**Photoelectrochemical cell measurements:** Photoelectrochemical measurements were performed in a three-electrode cell with a potentiostat/galvanostat (PG-stat) (Wona Tech, ZIVE SP1). Co$_3$O$_4$/FTO/glass, Ag/AgCl (KCl, 3 M), and platinum gauze were connected to the working, reference, and counter electrodes of the PG-stat, respectively. All PEC cell measurements were carried out in 0.1 M NaOH aqueous electrolyte pH 12.5 at room temperature. A white light source (5800 K, Bridgelux, ES Star Array, BXRA-56C0700-A) with a light intensity of 100 mW·cm$^{-2}$ was calibrated with a power meter (KUSAM-MECO, KM-SPM-11). Scan rates of 20 mV·s$^{-1}$ with a 0.1 mV step were set to record the linear sweep voltammetry (LSV), with the scan direction from positive to negative potentials in all cases. The measured potential vs Ag/AgCl were converted to the RHE to study the stability of the Co$_3$O$_4$ working electrode. A Mott–Schottky analysis of the photoelectrodes was performed at an ac amplitude of 10 mV and in a frequency range of 5 kHz to 500 Hz. The dc potential was scanned from 1.4 to −0.4 V vs RHE with a sampling interval of 25 mV. All the PEC measurements were performed in an Ar purging environment at room temperature with 40 mL of electrolyte.

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**Supporting Information**

Supporting Information File 1

Additional experimental data.

[https://www.beilstein-journals.org/bjnano/content/supplementary/2190-4286-9-228-S1.pdf]

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