Conducting-Polymer Nanocomposites as Synergistic Supports That Accelerate Electro-Catalysis: PEDOT/Nano Co$_3$O$_4$/rGO as a Photo Catalyst of Oxygen Production from Water

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Abstract: This work describes how conducting polymer nanocomposites can be employed as synergistic supports that significantly accelerate the rate of electro-catalysis. The nanocomposite PEDOT/nano-Co$_3$O$_4$/rGO is discussed as an example in this respect, which is specific for photo electro-catalytic oxygen (O$_2$) generation from water using light (PEDOT = poly (3,4-ethylenedioxythiophene); rGO = reduced graphene oxide). We show that the conducting polymer PEDOT and the conductive additive rGO may be used to notably amplify the rate of O$_2$-generation from water by the nano catalyst, Co$_3$O$_4$. A composite film containing the precise molar ratio 7.18 (C; PEDOT):1 (Co):5.18 (C; rGO) exhibited high photocatalytic activity (pH 12) for the oxygen evolution reaction (OER) at 0.80 V (vs. Ag/AgCl), with a current density of 1000±50 µA/cm$^2$ (including a photocurrent of 500 µA/cm$^2$), achieved after >42 h of operation under illumination with a light of intensity 0.25 sun. By comparison, the best industrial catalyst, Pt, yielded a much lower 150 µA/cm$^2$ under the same conditions. Oxygen gas was the sole product of the reaction.

Keywords: conducting polymer; reduced graphene oxide; photocatalysis; water-splitting; nanocomposite

1. Introduction

Electro-catalysis is a field of increasing importance due to the rapidly declining cost of renewable electricity. The National Renewable Energy Laboratory (NREL) (Golden, Colorado, USA) recently published data showing that the cost of electricity produced by renewable energy was expected to continue its sharp decline over the next decade, reaching $24/MWh for utility-scale solar power by 2025 and utility-scale onshore wind by 2030 [1]. Very low-cost electricity of this type may be expected to increase the demand for devices that utilize electro-catalytic electrodes, such as those used in water-splitting solar cells. The water-splitting reaction generating H$_2$ and O$_2$ gases follows the equation:

$$2H_2O \rightarrow 2H_2 + O_2 \quad (E^0 = 1.23 \text{ V})$$

In practice, a voltage in excess of 1.23 V is required to drive the reaction towards the production of gases.

As such, it is important to develop techniques that maximize the performance of nano-particulate electro-catalysts, which are typically deposited as thin films on electrode surfaces. One approach that has recently been developed by our research group in this respect involves the use of conducting polymers [2] and conductive additives as supports.

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that create synergies with the electro-catalyst to maximally accelerate the overall electro-catalytic rate [3–10].

In effect, the photo- (or)electro-catalyst is deposited in a thin film nanocomposite that contains within it very specific proportions of a uniformly dispersed conducting polymer and conductive additive. The conducting polymer provides a large number of electrical connections to the innumerable catalytic sites on the many surfaces of the catalyst nanoparticles, along the shortest possible connection pathways to the electrode, while the conductive additive decreases the resistance of those pathways and increases visible light absorbance [3–10].

The synergy arises in that no additional conducting polymer or conductive additive is used beyond the minimum required. This is necessary to ensure that the largest possible quantity of catalyst nanoparticles is present, yielding the highest possible catalytic activity. In this way, the competing requirements of maximum catalytic loading, and the best electrical connection to each catalytic site, along the shortest and most conductive pathway to the electrode, are simultaneously achieved [3–10].

In the present work we describe the application of this approach to an example system that has not been previously studied or reported, namely the use of the light-absorbing conducting polymer poly (3,4-ethylenedioxythiophene) (PEDOT), combined with the conductive additive reduced graphene oxide, rGO, in the amplification of photo-electro-catalytic oxygen production from water by the well-known water oxidizing electro-catalyst nano Co$_3$O$_4$.

We show that a thin film of Co$_3$O$_4$ deposited on an electrode as a nanocomposite with PEDOT and rGO in the molar ratio of 7.18 (C; PEDOT):1 (Co):5.18 (C; rGO) exhibits high photo catalytic activity (pH 12) for the oxygen evolution reaction (OER) at 0.80 V (vs. Ag/AgCl), with a current density of 1000 ± 50 µA/cm$^2$ (including a photocurrent of 500 µA/cm$^2$), achieved after >42 h of operation under illumination with light of intensity 0.25 sun. These conditions were selected as the most favorable for oxygen generation from water, at which PEDOT does not degrade. In comparison, the most widely used and highest performing industrial catalyst, Pt, has a significantly lower activity under the same conditions, producing a mere 150 µA/cm$^2$. Oxygen gas was the sole product of the reaction.

2. Materials and Methods

2.1. Electrode Preparation

The methodology for fabricating the thin-film PEDOT/nano Co$_3$O$_4$/rGO nanocomposite electrodes was as described previously [4], with GO incorporated instead of MWCNTs. Co$_3$O$_4$ nanoparticles with nominal size of 25 nm were provided by Skyspring Nanomaterials. The monomer EDOT was provided by Sigma-Aldrich and further purified via distillation. The GO was prepared as described previously [3]. Following formation of the thin film composites containing GO, the GO in the composite was reduced to rGO, as described previously [3], by cyclic voltammetry (CV) over the range –1.1 V to –0.8 V (vs. Ag/AgCl) in 0.2 M Na$_2$SO$_4$ with the pH adjusted to 12.

2.2. Electro-Catalysis Measurements

Measurements of the thin-film PEDOT/nano Co$_3$O$_4$/rGO nanocomposite electrodes as oxygen evolution photo electro-catalysts were carried out as described previously in 0.2 M Na$_2$SO$_4$, adjusted to pH 12, with an external bias of 0.8 V vs. Ag/AgCl applied [3,4]. The electrodes were illuminated with a Solux halogen bulb having a low light intensity (0.25 sun). The light was filtered through a band pass filter (315–710 nm) to exclude any infrared radiation. Measurements were carried out with a Pt mesh counter electrode and a saturated Ag/AgCl reference electrode. The walls of the cell were quartz. An EDAQ Potentiostat e-corder 466 potentiostat was used to record data.
2.3. Gas Sensing Experiments

The gaseous products of the electrocatalysis were collected in a specially design electrochemical cell and passed along stainless-steel tubes to a dedicated Shimadzu GC-8A gas chromatograph (GC) with a thermal conductivity detector (TCD), as described previously [3,4]. The identity of the gases was determined by their retention times on the GC column used. Prior to measurements, the cell and GC loop were purged for at least 6 h with pure argon.

2.4. Physical Characterization of the PEDOT/nano Co$_3$O$_4$/rGO Nanocomposite Thin Films

Powder XRD was carried out with a GBC MMA XRD (Cu K$_\alpha$ radiation with $\lambda = 1.5418$ Å; scan rate of 2% min in the range of 8–80$^\circ$) at −40 kV and 25 mA, respectively. XPS measurements were carried out on a PHI 660 using a monochromatic Mg K$_\alpha$ X-ray as a beam source. SEM images and EDX was carried out with a Tescan Vega 2 Cz. Thickness was measured with a Vecco Dektak 150 profilometer. A HG29315 Jandel four-point probe (Jandel, Leighton Buzzard, UK) was used to determine the electrical resistivity of the films. Elemental analysis was carried out at the Campbell Microanalytical Laboratory at Dunedin University, New Zealand.

2.5. UV-Visible Absorbance of Nanocomposite Thin Films

Films were deposited on a glass slide and their UV-Visible spectra recorded with a UV-1800 SHIMADZU2 (Shimadzu, Kyoto, Japan, Analytical and measuring intstruments) in the range 400–800 nm.

3. Results and Discussion

3.1. Fabrication of the PEDOT/nano Co$_3$O$_4$/rGO Nanocomposites

The electrodes of this study were fabricated by coating 4.2 cm$^2$ fluorine tin oxide (FTO) glass slides, or flexible indium tin oxide (ITO)-coated polyethylene terephthalate films (‘ITO film’), with PEDOT/nano Co$_3$O$_4$/rGO nanocomposites, using vapor-phase polymerization of PEDOT [3,4].

Polymerization mixtures containing varying quantities of nano Co$_3$O$_4$ and graphene oxide (GO), along with a fixed, small quantity of Fe$^{3+}$ oxidant, were, first, spin-coated as thin films onto the FTO-glass or flexible ITO-PET [3,4]. The resulting coated electrodes were then placed in a chamber filled with the vapor of the monomer, 3,4-ethylenedioxythiphene (EDOT) and heated at 60 °C for 1 h. During that time, the EDOT vapor was polymerized to PEDOT by the Fe$^{3+}$ on the electrode surface, creating the PEDOT/nano Co$_3$O$_4$/rGO nanocomposites as thin films on the FTO-glass or flexible ITO-PET. The electrodes were thereafter thoroughly washed with ethanol to remove all of the Fe$^{2+}$ formed from the Fe$^{3+}$ oxidant during the polymerization and left to dry overnight. Copper wires were then attached to the conducting FTO or ITO surface using conducting silver paint and the electrodes were subjected to cyclic voltammetry in 0.2 M Na$_2$SO$_4$, with the pH adjusted to 12 to reduce the GO to rGO, as described previously [3] (see also Figure S2); rGO is more conductive than GO.

3.2. Electro-Catalysis by the PEDOT/nano Co$_3$O$_4$/rGO Nanocomposites

The resulting PEDOT/nano Co$_3$O$_4$/rGO nanocomposite-coated electrodes were tested for their capacity for catalyze oxygen generation from water in a three-electrode setup with a Pt mesh counter electrode and a Ag/AgCl reference electrode [3,4].

Previous studies [3,4] established that the optimum quantity of nano Co$_3$O$_4$ that could be included in such a thin film was obtained when 110 mg of nano Co$_3$O$_4$ was present in the polymerization mixture that was spin-coated onto the FTO-glass or flexible ITO-PET substrate.

Studies thereafter examined the optimum quantity of rGO to incorporate into the nanocomposite. Figure 1 depicts the O$_2$-producing electro-catalytic performance from water of nanocomposite electrodes with 1.0–4.0 mg of rGO present, with and without illumination with light. The conditions employed for the comparative tests in Figure 1
were used throughout this study, as they are the most favorable for oxygen production that PEDOT can stand without degradation [3,4].

As can be seen, the best performance under light illumination was achieved by the nanocomposite containing 2.0 mg of rGO, which yielded a maximum current density of \( \approx 600 \, \mu A/cm^2 \), including a photocurrent of \( \approx 300 \, \mu A/cm^2 \).

On this basis, further studies employed nanocomposites prepared using 110 mg of nano Co\(_3\)O\(_4\) and 2.0 mg of rGO. These films were typically around 0.62 \( \mu m \) thick and exhibited a conductivity of 8.56 S/cm (on a glass slide).

For comparative studies, we next prepared samples of the FTO glass sputter-coated with a 100 \( \mu m \) thick layer of Pt, which is the most widely used catalyst for this reaction. The resulting electrodes were tested as comparative controls. Control samples, coated only with PEDOT or PEDOT containing 2.0 mg of rGO, were also prepared.

To make an accurate comparison of its catalytic performance, PEDOT/nano Co\(_3\)O\(_4\)/rGO nanocomposite (110 mg Co\(_3\)O\(_4\); 2.0 mg rGO in the polymerization solution) was also deposited onto the Pt-coated FTO substrate. This allowed for a comparison that took into account the lowered sheet resistance of the substrate after it was coated with Pt.

Figure 2 depicts the catalytic performance of the resulting PEDOT/nano Co\(_3\)O\(_4\)/rGO nanocomposite on Pt/FTO for oxygen production from water (Figure 2b), as compared to the control Pt/FTO (Figure 2a) and control PEDOT/FTO (Figure 2c) (which was the same as the control PEDOT/FTO containing 2.0 mg of rGO). As can be seen, the PEDOT/nano Co\(_3\)O\(_4\)/rGO nanocomposite coated on Pt/FTO produced a total current of 1000 ± 50 \( \mu A/cm^2 \), including a photocurrent of 490–500 \( \mu A/cm^2 \) (Figure 2b). This was \( \approx 7 \)-fold larger than the control, bare Pt coated FTO slide (Figure 2a) and \( \approx 20 \)-fold higher than the PEDOT control (Figure 2c).
Figure 2. Electro-catalytic performance in oxygen generation from water over 1 h of operation, with and without light illumination (0.25 sun), of FTO glass slide electrodes coated with (a) bare Pt (control); (b) Pt that was subsequently coated with PEDOT/nano Co3O4/rGO, where the polymerization mixture used to fabricate the nanocomposite contained 110 mg of nano Co3O4 and 2.0 mg of rGO; and (c) PEDOT only (control). Conditions: applied bias on the electrodes of 0.80 V (vs. Ag/AgCl) in 0.2 M Na2SO4 (pH 12) (* = ‘light on’, # = ‘light off’).

Over 42 h of continual operation, the PEDOT/nano Co3O4/rGO on Pt/FTO displayed remarkable robustness, even when the illuminating light was periodically turned off and on (Figure 3). The current density under illumination was 950–1050 µA/cm² over the testing period.

Figure 3. Electro-catalytic performance in oxygen generation from water, with and without light illumination (0.25 sun), of PEDOT/nano Co3O4/rGO nanocomposite deposited on Pt/FTO, where the polymerization mixture contained 110 mg of nano-Co3O4 and 2.0 mg of rGO; and (c) PEDOT only (control). Conditions: applied bias on the nanocomposite electrode of 0.80 V (vs. Ag/AgCl) in 0.2 M Na2SO4 (pH 12) (* = ‘light on’, # = ‘light off’).

The above PEDOT/nano Co3O4/rGO nanocomposite was also deposited on a flexible ITO-PET substrate. Chronocoulometry produced a current density of 305–317 µA/cm² under light illumination (Figure 4). The lower performance of the flexible coated ITO-PET electrode was due to the sheet resistance of the ITO, which was higher than that of FTO and very much higher than Pt-coated FTO.
3.3. Gas Produced by the PEDOT/nano Co₃O₄/rGO Nanocomposite

The gas bubbles produced by the PEDOT/nano Co₃O₄/rGO nanocomposite on Pt/FTO, under the conditions described in Figure 2, were collected using a custom-built cell, which has been described elsewhere [3,4]. Gas chromatography confirmed that the gas produced was oxygen (albeit contaminated with tiny quantities of hydrogen from the cathode) (Figure S1; Supplementary data).

3.4. Characterization of the PEDOT/nano Co₃O₄/rGO Nanocomposite

The most active PEDOT/nano Co₃O₄/rGO nanocomposite was characterized using powder x-ray diffraction (XRD), elemental analysis, scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), and electrochemical impedance spectroscopy (EIS).

Powder XRD (Figure 5) revealed peaks at 2θ = 18.9°, 31.26°, 36.9°, 38.52°, 44.82°, 55.46°, 59.48°, and 65.34° that corresponded to the nano Co₃O₄ cubic space group Fd̅3m [11–13]. Two other peaks at 25.91° and 26.48° were due to the rGO and PEDOT, respectively (Figure S2) [2,5].
Elemental analysis of the PEDOT/nano Co$_3$O$_4$/rGO film indicated a ratio of 17.0% Co, 11.34% S, and 44.09% C, which corresponded to a molar ratio of 7.18 (C; PEDOT):1 (Co):5.18 (C; rGO).

SEM (Figure 6) showed that the nanocomposite had a porous structure, with EDX confirming a uniform dispersion of the components; namely, PEDOT (shown by S, top left), rGO and PEDOT (shown by O; top second-from-left), Co$_3$O$_4$ (shown by Co, top third-from-left), and rGO (shown by C, top right).

An XPS analysis of the PEDOT/nano Co$_3$O$_4$/rGO nanocomposite is provided in Figure S3. Peaks attributable to S 2p, O 1s, C 1s, Co 2p, and O 1s, respectively, were identified. The O 1s and C 1s spectra derive from PEDOT and rGO, while the S 2s is derived from the PEDOT only.

Electrochemical impedance spectroscopy (EIS) (Figure 7) (EIS) of the most active PEDOT/nano Co$_3$O$_4$/rGO nanocomposite on Pt/FTO, and the control electrodes, was carried out at the above-mentioned working conditions at frequencies of 10–10,000 Hz. These studies confirmed that the nanocomposite had low ohmic resistance ($R_{el}$), adsorption resistance ($R_{ad}$), diffuse layer capacitance ($C_{dl}$), catalytic charge transfer resistance ($R_{CT}$), and capacitance expressed in terms of a constant phase element ($Q_{CPE}$, $n_{CPE}$, and $C_{CPE}$) (Table 1). These results confirmed and defined the high catalytic activity for the OER by the PEDOT/nano Co$_3$O$_4$/rGO composite. (For more detail, see the Supplementary data).
Figure 7. Electrochemical Impedance Spectroscopy: (a) equivalent circuit, (b) full Nyquist plot, (c) Nyquist plot of high frequency region only, (d) Tafel plots, of: (i) PEDOT/nano Co$_3$O$_4$/rGO illuminated with light, (ii) PEDOT/nano Co$_3$O$_4$/rGO without light illumination, (iii) Pt control, (iv) PEDOT control illuminated with light, and (v) PEDOT control without light. The individual points in (b,c) display measured data, while the solid lines display data modelled using the equivalent circuit depicted in (a).
Table 1. Data from EIS; $R_{el}$ = ohmic resistance, $R_{ad}$ = adsorption resistance, $C_{dl}$ = diffuse layer capacitance, $R_{CT}$ = catalytic charge transfer resistance. $Q_{CPE}$, $n_{CPE}$, and $C_{CPE}$ describe the capacitance expressed in terms of a constant phase element. The last two columns depict data from the Tafel plot studies in Figure 7d: slope A (in mV/decade), exchange current density, $i_o$ (in mA/cm$^2$). ('dark' = without light illumination; 'light' = with light illumination).

| Sample                        | $R_{el}$ $\Omega$ cm$^2$ | $R_{ad}$ $\Omega$ cm$^2$ | $C_{dl}$ $\mu$F cm$^{-2}$ | $R_{CT}$ $\Omega$ cm$^2$ | $Q_{CPE}$ $\mu$F cm$^{-2}$ | $n_{CPE}$ | $C_{CPE}$ $\mu$F cm$^{-2}$ | $A$ mV/dec | $i_o$ $\mu$A cm$^{-2}$ |
|-------------------------------|---------------------------|----------------------------|-----------------------------|---------------------------|----------------------------|------------|-----------------------------|-------------|------------------------|
| PEDOT (dark)                  | 18.89                     | 420.3                      | 16.1                        | 148.3                     | 0.07                       | 0.88       | 0.01                        | 277         | 20.60                  |
| PEDOT (light)                 | 17.26                     | 400.1                      | 20.9                        | 122.9                     | 0.14                       | 0.88       | 0.02                        | 272         | 25.88                  |
| Pt only                       | 19.73                     | 270                        | 9.89                        | 120.7                     | 0.06                       | 0.92       | 0.021                       | 250         | 50.46                  |
| Pt/PEDOT/Co$_3$O$_4$/rGO (dark)| 16.90                     | 145                        | 3.54                        | 55                        | 2.84                       | 0.89       | 0.85                        | 97.4        | 4.56                   |
| Pt/PEDOT/Co$_3$O$_4$/rGO (light)| 16.60                    | 128                        | 4.04                        | 51                        | 3.30                       | 0.89       | 1.06                        | 93.7        | 4.17                   |

3.5. Synergies in the PEDOT/nano Co$_3$O$_4$/rGO Nanocomposite

The last two columns of Table 1 provide relevant Tafel plot data of the most active PEDOT/nano Co$_3$O$_4$/rGO nanocomposite on Pt/FTO, and the control electrodes (see the Supplementary data for more information). As can be seen, the PEDOT/nano Co$_3$O$_4$/rGO produced the lowest Tafel slopes of 93.7 mV/dec and 97.4 mV/dec, with and without light illumination, respectively. These results are lower than the comparable slopes of the Pt and PEDOT control films. The exchange current densities ($i_o$) of the PEDOT/nano Co$_3$O$_4$/rGO, with and without light illumination, can also be seen to improve upon the comparable control PEDOT film by $\approx$4–6 fold. It is likely that rGO provided electrically conductive channels between PEDOT and nano Co$_3$O$_4$, increasing the lifetime of holes, and resulting in an enhanced photocatalytic activity. We previously studied the synergistic role of multiwalled carbon nanotubes (CNTs) in PEDOT-nano Co$_3$O$_4$ films. It can be concluded that rGO played a similar role here to that of the CNTs previously in the overall photocatalytic activity. In addition, the use of rGO here boosted the water-splitting durability compared to PEDOT/nano Co$_3$O$_4$/CNT nanocomposite film.

This is a smaller improvement than a previous study of PEDOT/nano Co$_3$O$_4$ nanocomposite in which multi-wall carbon nanotubes (MWCNTs) were used as the conductive additive [4]; that system yielded a 15-fold improvement when 110 mg of nano Co$_3$O$_4$ and 2.0 mg of the conductive additive was used in the polymerization solution [4]. Accordingly, the synergistic effect created by using rGO as conductive additive was smaller than that produced by using MWCNTs under comparable conditions.

This can be understood by considering the elements that create the synergy; namely, (i) the PEDOT, which creates innumerable electrical pathways between the electrode substrate and the many catalytic sites on the Co$_3$O$_4$ nanoparticles; and (ii) the conductive additive, which increases the conductivity of those pathways. The higher conductivity of the MWCNTs per unit weight relative to the rGO, thus, had the effect of decreasing the resistance of the pathways to the catalytic sites on the nano Co$_3$O$_4$, and this improved the overall performance.

The way to maximize the synergies in a nanocomposite of this type, i.e., to maximize the extent of the electro-catalytic acceleration, is therefore to employ component materials that perform their relative functions as best possible. That is, the greatest acceleration in electro-catalytic performance will be achieved by using: (i) conducting polymers that provide the best electrical connectivity to the catalytic sites, (ii) catalysts with the largest number of the most active catalytic sites possible, and (iii) conductive additives with the greatest conductivity.

3.6. Faradaic Efficiency of PEDOT/Nano-Co$_3$O$_4$/rGO

The output gas of PEDOT/nano-Co$_3$O$_4$/rGO composite during water-splitting, with and without light illumination, was passed through a gas chromatograph (GC). Using pure oxygen as the calibration gas, the output gas was confirmed to contain 61.2% and 62.1% oxygen, without and with light illumination, respectively, corresponding to a Faradaic efficiency of 61.2–62.1%.

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4. Conclusions

In this work, we have described and demonstrated how tri-component nanocomposite supports may be used to accelerate and amplify the performance of electro-catalysts. In particular, we have shown that a thin film nanocomposite of PEDOT/nano Co$_3$O$_4$/rGO can be made more active than a standard Pt film catalyst. This can be achieved even without the best possible conductive additive (rGO vs. MWCNTs). The key is to optimize the molar ratios of the different components to thereby maximize their synergistic interaction with each other. Thus, PEDOT/nano Co$_3$O$_4$/rGO in the very specific molar ratio of 7.18 (C; PEDOT):1 (Co):5.18 (C; rGO) exhibited excellent OER activity over >42 h of operation under a light illumination of 0.25 sun. GC analysis demonstrated that oxygen was the only gas generated by the electrode. SEM/EDX showed that the film had a porous structure, with evenly distributed components. XPS confirmed the presence of the PEDOT, rGO, and Co$_3$O$_4$ components. Finally, the Tafel data of the active PEDOT/nano Co$_3$O$_4$/rGO confirmed the high catalytic OER activity of the nanocomposite.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/jcs5090245/s1, Figure S1: Gas chromatography traces of gases collected from PEDO/nano Co$_3$O$_4$/rGO on FTO electrode, Figure S2: XRD of GO and rGO films, Figure S3: XPS spectra of PEDOT/nano-Co$_3$O$_4$/rGO showing various binding energy regions; peaks representing the depicted transitions are shown, along with simulations (solid lines) and measured data (individual points). C 1s spectra and O 1s derive from both PEDOT and rGO while S 2p derives from PEDOT only and Co 2p derives from nano-Co$_3$O$_4$, Figure S4. UV-Vis spectra of rGO, PEDOT, and PEDOT/nano-Co$_3$O$_4$/rGO.

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