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Photocatalytic, Oxygen-Generating PEDOT/Nano-Ni Composite film with Sustained High Activity

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Abstract:

Composite PEDOT films, prepared using vapour phase polymerisation incorporating with nanoparticulate Ni ('nano-Ni') on FTO glass have been studied as photoelectrocatalysts of water oxidation in 0.2 M Na_2SO_4 electrolyte at different pH. The PEDOT/nano-Ni Films proved to be active at high pH generating current densities at 0.80 V (vs Ag/AgCl) of 0.655 mA/cm^2 (including a photocurrent of 0.4 mA/cm^2) under light illumination of 0.25 Sun. A variety of techniques were used to study and characterized the films, including: cyclic voltammetry, chronoamperograms, gas chromatography and scanning electron microscope.

Keywords: Water splitting, Oxygen evolution reaction (OER), PEDOT, nano-Ni

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تحضير وتشخيص المركب الغشائي PEDOT/Nano–Ni كحفاز ضوئي لتوليد غاز الاوكسجين ذو الكفاءة المستدامة

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الملخص

تمت دراسة أغشية PEDOT المركبة ، المحضرة باستخدام بلمرة الطور البخاري المحضر مع جزيئات النانو ("nano–Ni") على زجاج FTO كمحفزات كهروضوئية لأكسدة الماء في 0.2 M Na_2SO_4 بالكهرباء عند درجة حموضة مختلفة. أثبتت أفلام PEDOT / nano–Ni أنها نشطة عند درجة حموضة عالية تولد كثافات تيار عند 0.80 فولت (مقابل Ag / AgCl) تبلغ 0.655 مللي أمبير/ سم^2 (بما في ذلك تيار ضوئي يبلغ 0.4 مللي أمبير / سم^2) تحت إضاءة ضوئية تبلغ 0.25 شمس. تم استخدام مجموعة متنوعة من التقنيات لدراسة وتمييز الأفلام ، بما في ذلك: قياس الفولتميتر الدوري ، كرونومبيروجرامس ، كروماتوغرافيا الغاز والمسح الإلكتروني المجهر.

1. INTRODUCTION

Renewable energy such as sunlight, wind, rain, tides, waves, and geothermal heat, are promising as alternative energy resources and could meet energy demands, combat climate change and fossil fuel depletion [1]. Sunlight-driven water splitting is a type of renewable energy that produces H_2 and O_2 ($H_2O \rightarrow H_2 + 1/2\ O_2$). It occurrence in photoelectrochemical cells (PEC) has been widely investigated since Fujishima and Honda's discovery in 1972 of production of H_2 from TiO_2 [2, 3]. However, water splitting is an uphill chemical reaction that requires a standard electrochemical potential of 1.23 V vs NHE. In practice, substantially higher potentials are required due to the overpotentials for the hydrogen and oxygen evolution reactions [4]. The efficiency of water splitting systems depend on the surface area, shape and size of catalysts materials that are used [5], the electrolyte types and pH, [6] and the external biases that are applied [7]. PECs have some favourable practical outcomes including; low cost, environmental friendly, stability, wide visible absorption, and band position [8, 9].

Conductive polymers (CP) have unique properties that make them suitable for solar water-splitting applications. These include: conductivity, permeability to water, low-cost, environmental non-toxicity, electrochemical stability, useful light absorption, ready combination with other materials, excellent electron transfer properties, and uncomplicated preparative methods, amongst others. This diversity and utility impart CPs with great promise in the catalytic generation of hydrogen and/or oxygen from water under illumination by sunlight. The conversion efficiency of such "polymer" solar cells is, however, still low when compared with inorganic semiconductors [10]. Poly(3,4-ethylenedioxythiophene (PEDOT) is considered to be the best available CP in terms of conductivity, processability, transparency to visible light, stability, and fast electrochemical switching [11]. A significant study wherein PEDOT was used as a "stand-alone", light–assisted water oxidation catalyst has been carried out by Chen and co-workers [13] when they deposited PEDOT on ITO-PET sheets by vapour phase polymerization (VPP) with, and, without, the incorporation of the anionic sulfonated Mn-porphyrin (**1**). PEDOT without **1** exhibited a blue-white colour, while PEDOT-**1** displayed a green colour having increased absorption peaks and higher photocurrent associated with O_2 formation from water. One possible way to enhance PEC performance is to utilize two or more chemical materials with different spectral responses to achieve a higher overall utilization of solar energy. To the best of our knowledge no study has investigated this option as yet for water splitting PEC interfaces between Ni as nanoparticles (NP) and PEDOT. Herein, we investigate a PEC comprising PEDOT that incorporated different ratios of nano-Ni. The results confirmed that an increase of nano-Ni ratio or higher pH enhanced PEC performance. Gas Chromatography confirmed evolution of O_2 gas, while EDX spectrum of scanning electron microscope image exhibited a uniform mapping distribution.

2. EXPERIMENTAL

2.1 Materials and method

The following materials were used: Fluorine-doped tin oxide (FTO) slides, glass microscope slides; iron(III) p-toluenesulfonate (Fe(III)-pTS); 3,4-ethylenedioxythiophene (EDOT) FTO and glass substrates were cleaned using a PLAMAFLO PDC-FMG Plasma cleaner and a DIG UV PSD PR SERIES digital UV Ozone cleaner. Sonication was carried out using a B2500R-MTH sonicator. Spin-coating onto the substrates was carried out using a WS-400B-6NPP/LITE spin-coater. Scanning Electron Microscopy (SEM) images were

taken using a JEOL 7500 FESEM. pH measurements were done with an Oakton pH /conductivity meter.

2.2 Preparation of PEDOT, PEDOT/nano-Ni, on FTO-coated glass slides

Uncoated glass and FTO-coated glass slides were immersed in acetone within a TLC chamber. The baths with the immersed slides were sonicated for 90 min, the slides were washed with water and dried by blowing air over them. The FTO and uncoated glass slides were then labelled. All slides were thereafter treated in a digital ozone-UV cleaner for 20 min to remove organic contaminants. The slides were then cleaned in a plasma cleaner in order to functionalize groups on the slide's surface with which to fix the coated chemical solutions during spin-coating. The FTO and glass substrates were heated to dryness on an IKA® RCT basic hotplate at 60 °C.

To prepare PEDOT, PEDOT/nano-Ni, 100 mg of Fe(III)-PTS was dissolved in 1.2 mL absolute ethanol. Then the required amount of Ni-nano (as applicable) was added gradually with magnetic stirring continuing for 2.5 h. The resulting dispersion (100 µL) was dropcasted onto the slide surface using a micropipette. The slides were then spun at 2000 revolutions per min (rpm) for 180 s. After spin-coating, the sample was quickly transferred to a hotplate, where it was dried at 60 oC for 15 min. Vapour phase polymerisation was carried out in a separate conical flask (500 mL capacity), equipped with a rubber stopper containing a crocodile clip suspended above the bottom of the flask. EDOT (0.450 mL) was placed in the flask and the dried, spin-coated FTO or uncoated glass substrates were held above the EDOT solution by the crocodile clip, with the stopper in place. The stoppered conical flask was then placed in an oven at 60^{o} C for 60 min, during which time the EDOT vapour polymerised into PEDOT polymer on the slide surface. After polymerization was complete, the sample was removed, washed thoroughly with ethanol, and then left to dry overnight. The resulting dried FTO-coated samples were converted to usable electrodes by attaching a copper wire to the FTO surface with conductive silver paint and epoxy resin. When the silver paste was fully solidified, epoxy glue was used to cover the contact area of the wire as well as any exposed clean FTO glass surface

2.3 Studies of PEDOT and PEDOT/Nano-Ni, on FTO as OER Photocatalysts.

PEDOT and PEDOT/nano-Ni were employed as working electrodes within a fully-enclosed quartz cell (5 x 5 x 5 cm) placed inside a closed cabinet that comprised a Faraday cage. A Pt mesh (1 x 2 cm) was used as the counter electrode. A BASi Ag/AgCl aqueous salt bridge (KCl, 3 M) served as reference electrode. The electrolyte employed was a 0.2 M Na_2SO_4 aqueous solution. The electrolyte was bubbled with N_2 gas for 30 min before each experiment and maintained under an N_2 atmosphere during the experiments. Linear sweep voltammetry (LSV), cyclic voltammetry (CV) and chronoamperograms (CA) were performed using an EDAQ466 potentiostat. Where applicable, the sample was illuminated with a SoLux daylight MR16 halogen light bulb (12 V, 50 W, 24o; ca. 0.25 sun intensity) with bandpass filter (315-710 nm).

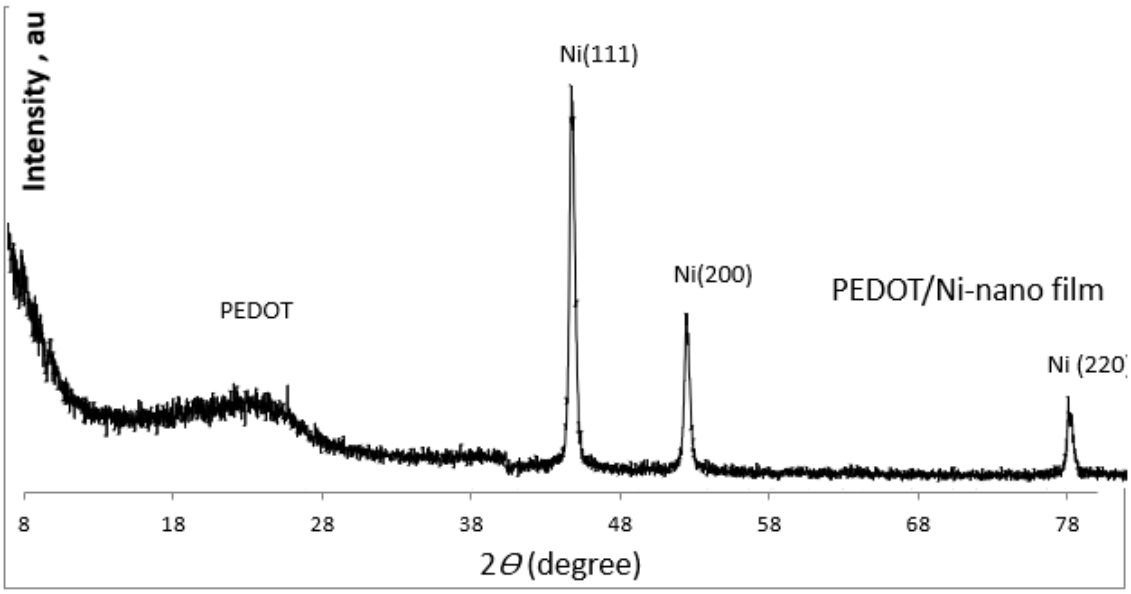
2.4 Gas Analysis Studies

Gas analysis was performed via a custom-built apparatus. The apparatus comprised of a fully-enclosed electrochemical cell containing two sealed, half-cells whose electrolytes were separated only by a Nafion 117 proton exchange membrane (5 x 4 cm). The one half-cell contained the working electrode sample and a Ag/AgCl reference electrode. The other half-cell contained the Pt mesh counter electrode. One wall of the former half-cell was a quartz sheet. Illumination from the above light source was passed through the quartz sheet onto the working electrode. The incident light was filtered with the above bandpass filter. The electrodes were connected to a CHI potentiostat. The gas outlets for the working and counter electrode half cells were connected with gas-tight polymer and stainless steel tubing to sample loops connected to a dedicated Shimadzu GC-8A gas chromatograph. 0.2 M Na2SO4 adjusted to pH 12 by adding KOH.

3. Results and Discussion

3.1 Studies of PEDOT and PEDOT/nano-Ni on FTO

In the first stage of this study XRD spectra of PEDOT/nano-Ni film was examined. As can be seen in Figure 1 PEDOT showed broad peaks $2\theta = 17\text{-}28^{O}$ due to carbon crystalline structure as will as there is a little sharp peak at 26.23^{O} due to the reflection of intermolecular of PEDOT polymer structure. While Ni- nano particles shows three peaks presence of PEDOT pattern peaks at $2\theta = 44.5^{O}$, 52.7^{O} and 76.3^{O} due to Ni(III), Ni(200) and Ni(220) pattern [12].



Secondly we examined the cyclic voltammogram (CV) of thin-films of vapour-phase polymerized PEDOT at different pHs on FTO glass, as water oxidation electro- and/or photo-catalyst in 0.2 M Na_2SO_4 aqueous solution with and without illumination by light from a SoLux daylight MR16 halogen light bulb (ca. 0.25 sun intensity). As can be seen in Figure 1(a), firstly, the current density and the onset potential of the PEDOT film increased with an increase of the pH. For example, the current density of the PEDOT increased five times when the pH increased from 7 to 12. Secondly, at each pH, when these films exposed to the light, the current density and the onset potential were enhanced. For example, at pH 12 when the PEDOT film was exposed to light, the current increased from 73 to 98 µA/cm2. In the second stage of this study, we examined PEDOT/nano-Ni film with a minimum amount of nano-Ni (5 mg of nano-Ni in polymerization solution)). As can be seen in Figure 1(b), these films exhibited further increases in the current density but less in the onset potential that can be seen in PEDOT film at same pH.

The next step of this research was to examine the chronoamperometric effect and the reproducibility of the photocurrents of PEC performance when the ratio of nano-Ni concentration further increased in polymerisation solution at pH 12. As can be seen in Figure 1(c), the current density increased with higher nano-Ni concentration in the polymerisation solution. The light illumination also

significantly enhanced the current. For example, when 125 mg was added to polymerization solution, the resulting PEDOT/nano Ni film displayed an

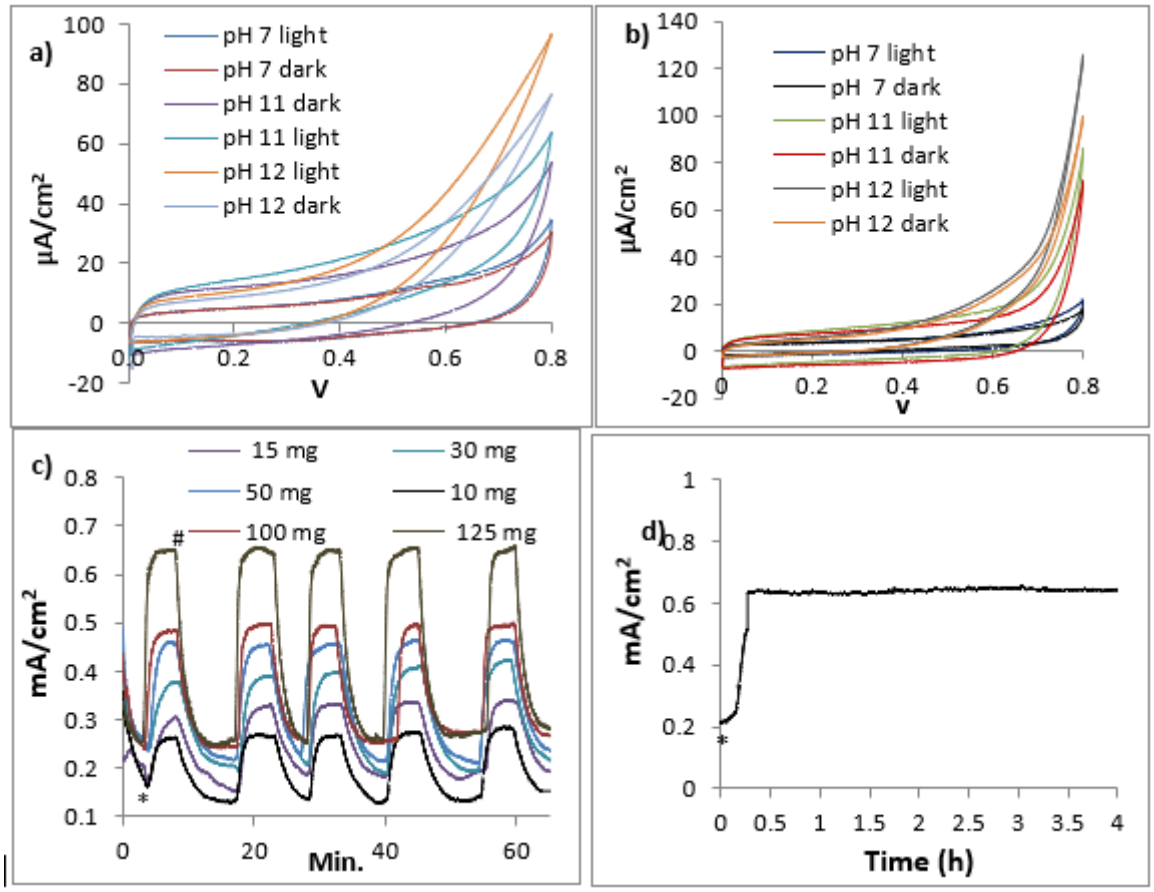


Figure 1. (a) CV of PEDOT under varying pH conditions. (b) CV of PEDOT/nano-Ni films with minimum concentration of nano-Ni (5 mg) with similar condition that applied in Fig.1(a). (c) Chronoamperograms of PEDOT/nano-Ni (with different nano-Ni concentration in polymerization solution) over 1 h of operation with and without light illumination of 0.25 sun (* =’light on’, #=’light off’). (d) Chronoamperogram over 6 h of operation.

increased current density, from 0.25 to 0.65 mA/cm2. While Figure 1(d) showed long-time of PEDOT/nano-Ni film operation under light for over 4 h.

3.2 GAS CHROMATOGRAPH ANALYSIS

THE GC TRACE ANALYSIS CONFIRMED THAT OXYGEN GAS WAS THE MAIN GAS EVOLVED IN THE DARK WITH A RATIO (%) 65: 35 (O_2: H_2) AND IN LIGHT TO BE 83:17 (O_2: H_2), SEE FIGURE 2.

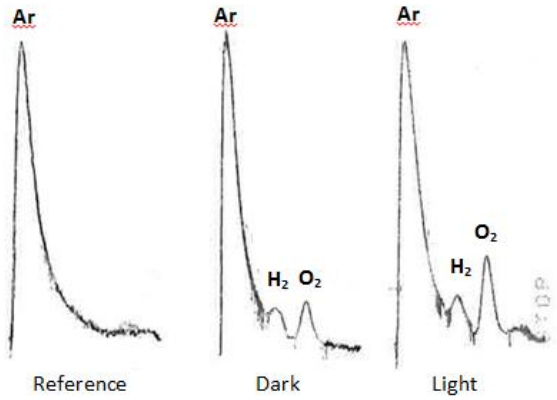


Figure 2. GC traces gas for the optimized performance of PEDOT/nano-Ni confirm O_2 gas was the main gas that evolved

3.3 Characterization of the PEDOT/Nano-Ni/rGO Electrode.

PEDOT/nano-Ni film morphology was investigated via scanning electron microscopy (SEM).The film was coated with 7 nm of Pt to increase the signal. Figure 3 shows an EDX-mapping peaks that confirms the distributions of Ni C, O, and S elements. It could be suggested that PEDOT/nano-Ni film when exposed to light in both CV and Chronoamperograms study, the π electrons in PEDOT were excited leaving holes at the nano-Ni surface. These holes stimulate water splitting enhances PEC performance. The GC trace confirms the oxygen evolution reaction peaks (see Figure 2).

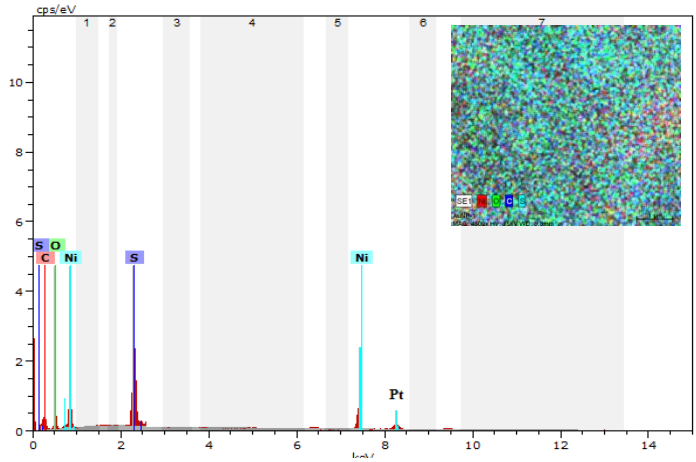


Figure 3. EDX spectrum of PEDOT/nano-Ni confirms the composition, the inset picture shows the uniform mapping distribution.

4. Conclusions

Cyclic voltammetry, photocurrent and conductivity measurements confirmed that nano-Ni particles incorporated into the conductive polymer PEDOT yielded a photocatalytic effect in which light illumination produced enhanced PEC performance. The quantity of nano-Ni present in the coating did not have a significant effect on the onset potential, but it did increase the photocurrent. In this respect, higher concentrations of nano-Ni did improve the PEC performance. It was conclude also when pH increases, the PEC performance dramatically improved. Further work be required to investigate the interfaces of reduce

Acknowledgements

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