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Characterisation of Porphyrinic Nanowires on Three Different Solid Substrates

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ABSTRACT

Integration of azo group into a polymer structure is one of the favourable options to enhance the conductivity and stability of a polymer. In this study, the azobenzene-linked nanowires were fabricated on three different solid electrodes by engaging electrooxidation to induce oxidative coupling. The formation of azobenzene-link in polymer structures was investigated and discussed. The X-ray photoelectron spectroscopy results revealed that the azobenzene-links were present in the polymeric structures. Besides that, the cyclic voltammograms proved the presence of azobenzene-linked and the nanowires shown to be stable upon repetitive scans. This study discovered that the nanowires formed a covalent bond on the surface of solid electrodes. Despite the differences in term of chemical composition between the electrodes, successful polymerisation had shown the potential of these electrodes to widely engage in areas such as energy storage and photonic devices. The photofunctionality and plausible mechanism for the photoelectric conversion of the electropolymerised porphyrin film were disclosed in this article.

Keywords: Azo-Linkage, One-Dimensional, Photocurrrent.

1. INTRODUCTION

Fabrication of molecular assemblies on various substrates involves various disciplines, for instance, nanomaterials, synthetic chemistry and surface engineering. Immobilisation of such assemblies on solid substrates can be performed either by a top-down or bottom-up method. Compared to top-down, bottom-up offered versatility in terms of controlling the structure of the polymers [1]. Nowadays, the modified solid substrates, such as silicon oxide and glassy carbon with molecular assembly known to be engaged in energy storage and conversion, electronics [2-3], biomedical [4], and so forth. Transparent solid substrates, such as quartz and indium-tin-oxide (ITO) offer good stability and excellent electrical conductivity, which are advantageous for molecular immobilisation and assembly. Both substrates display good optical transparency that allows optical read-out via various optical techniques, such as UV-vis spectroscopy and fluorescence spectroscopy, whereby unfortunate metal substrates can induce fluorescence quenching due to energy transfer to substrates. Transparent ITO has high transmittance and comparable conductive properties as metals which lead to numerous optoelectronic [6] and electrochemical applications [7]. On the other hand, the carbon materials, such as glassy carbon, (GC) were employed as substrates in electrochemical applications, such as in electrocatalysis [8] and electroanalysis [9]. GC is relatively cheaper than metals and offers wide potential window which is an advantage for electrochemical application [10].

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In order to secure distinct properties of solid electrodes, decent methods must be chosen to obtain successful immobilisation onto the surface of solid electrodes. Generally, the polymerisation can be carried out either through electrooxidative [11] or electroreductive [12] process. Between these two methods, electrooxidative is more favourable in generating porphyrin electropolymers than electroreductive because this method can form strong film attachment onto the solid surfaces [13]. Therefore, this method also has a high tolerance towards various types of porphyrin moiety. The polymerisation can be successfully achieved upon the formation of azobenzene linkage in polymer structures. The azo linkage is responsive towards irradiation of light and has high thermal stability which is favourable as an electron-conducting bridge [15-16]. For instance, the azo linkage is one of favourable functional group in developing liquid crystals [17]. To such degree, polymer with azobenzene linkage also displays photochromism [18] and photoconductivity [19], which leads to the fabrication of photonic devices [20]. This paper discusses the immobilisation strategies, surface characterisation techniques and the engagement of molecular films on ITO surfaces as photoanode in photocurrent generation.

2. MATERIALS AND METHODS

2.1 Materials

All chemicals were purchased and used as received from Kanto Chemical Co., Tokyo Chemical Industry Co., Ltd, or Wako Pure Chemical Industries, Ltd. [5,15-Di(4-aminophenyl)-10,20-diphenylporphyrinato] zinc(II)(**C1**) was synthesized according to previous studies with a few modifications [13]. The working electrode was fabricated from tin oxide (SO_2), indium-tin-oxide (ITO) on glass (5 Ω sq^{-1}) and glassy carbon (GC) rod (Tokai Carbon Co. Ltd.).

2.2 Methods

To conduct the photocurrent measurement, tetra-N butylammonium perchlorate, Bu_4NClO_4, was used as a supporting electrolyte and was purified by recrystallisation from ethanol, and dried in vacuo. Porphyrinic polymer wire **W1** was synthesised on GC, ITO and tin oxide (SnO_2) electrodes through electrooxidation of 2.0 mM **C1** in 0.1 Bu_4NClO_4-CH_2Cl_2. The photocurrent acquisition and electrode potential were controlled by an electrochemical analyser (ALS 750A, BAS Inc.). A monochromator (CT-10, JASCO Corporation) was used to monochromate the photon flux while the photon flux source was from a xenon lamp (MAX-302, Asahi Spectra Co., Ltd). The photon flux of the incident light was quantified by a photon counter (8230E and 82311B, ADC Corporation). The spectra were obtained by using an XPS microprobe (PHI 5000 VersaProbe, ULVAC-PHI, Inc.) and Al Ka (15 kV, 25 W) as X-ray source were then analysed with MultiPak (MultiPak Version 9.2.0.5 ULVAC-PHI, Inc.).

3. RESULTS AND DISCUSSION

The porphyrinic polymer wire W1 was synthesised and immobilised on GC, ITO and SnO_2 through electrooxidation method to study the electrochemical behaviour of different solid electrodes. Figure 1 shows a cyclic voltammogram of C1 in 0.1 M Bu_4NClO_4-CH_2Cl_2 in a repetitive redox process with a scan rate of 0.2 Vs^{-1}. The formation and growth of electroactive polymeric film were monitored by observing the increase of peak currents with the number of oxidation cycles. The shoulder peak next to broad anodic peak [21] was observed and identified as the oxidation of amino group [22] because the substituents had generally been oxidised before the porphyrin macrocyclic rings [23]. However, the conductivity of W1 started to decrease upon scan cycles of more than 50. Elongation of W1 up to certain length might decrease the electron transfer among porphyrin macrocycles. Greenish-yellow film was observed upon the immobilisation of W1 on ITO and SnO_2. The maximum peak was identified at ca. 0.5 V as shown in Figure 2 by engaging differential pulse voltammetry.

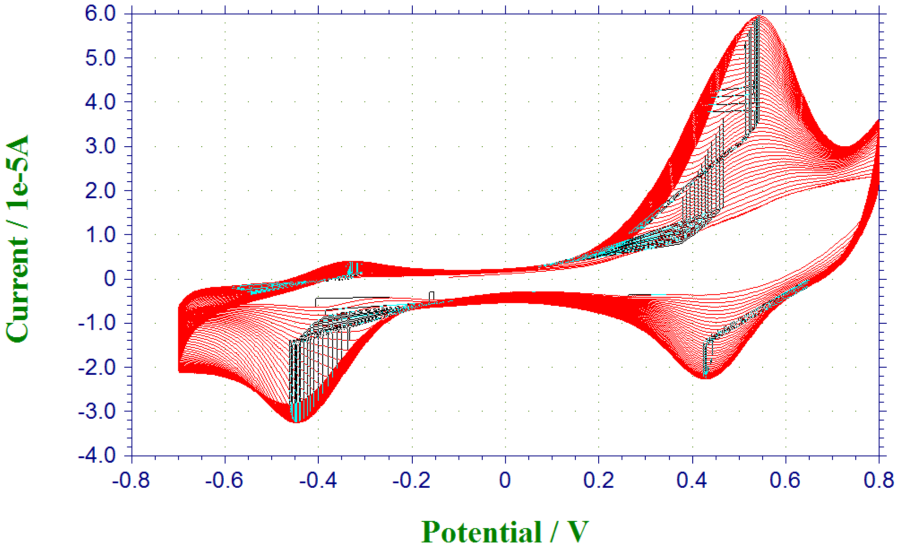

Figure 1. Repetitive scans of C1 in 0.1 M Bu_4NClO_4–CH_2Cl_2 at GC (from the1st to 50th cycles).

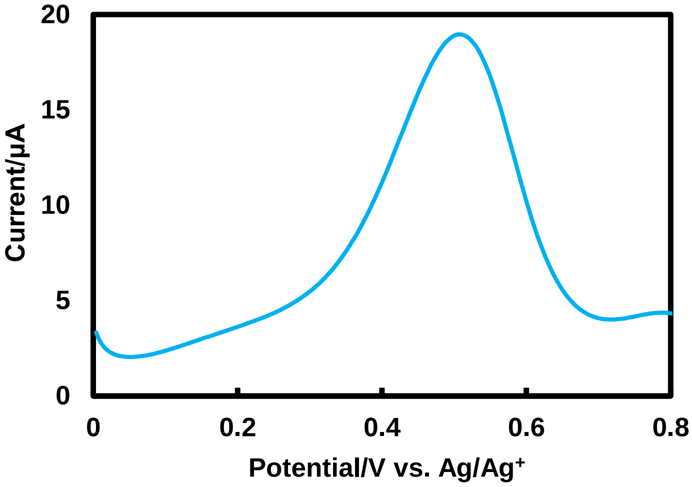

Figure 2. Differential pulse voltammogram for C1 in 0.1 M Bu_4NClO_4-CH_2Cl_2 at GC.

Although the composition of GC, ITO and SnO_2 were known to be different, all the electrodes exhibited similar electrochemical behaviour. Cyclic voltammograms in Figure 3 and Figure 4 showed identical oxidation peaks as in Figure 1. Unsaturated sp^2 carbons in GC facilitated W1 to be covalently attached to the surfaces while the differences between two transparent solid electrodes of ITO and SnO_2 only lied upon doping atoms. Hence, immobilisation of W1 on difference solid electrodes was successfully obtained and this indicated that monomer C1 were suitable to be engaged in modification of solid electrodes for various means. For instance, GC potential can be altered by coating the surface with electroactive film and subsequently engaged as energy storage [24].

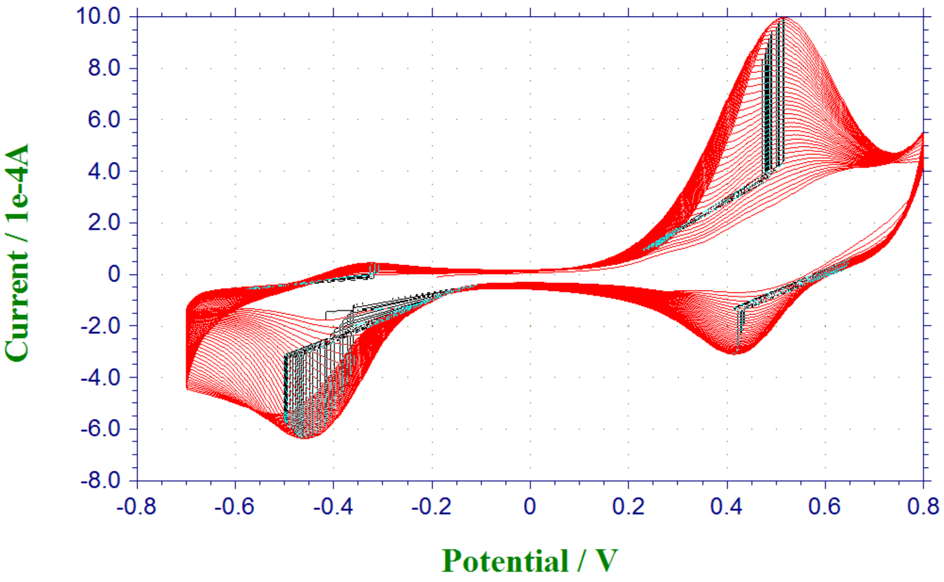

Figure 3. Repetitive scans of C1 (2mM) in 0.1 M Bu_4NClO_4–CH_2Cl_2 at ITO (from the1st to 50th cycles).

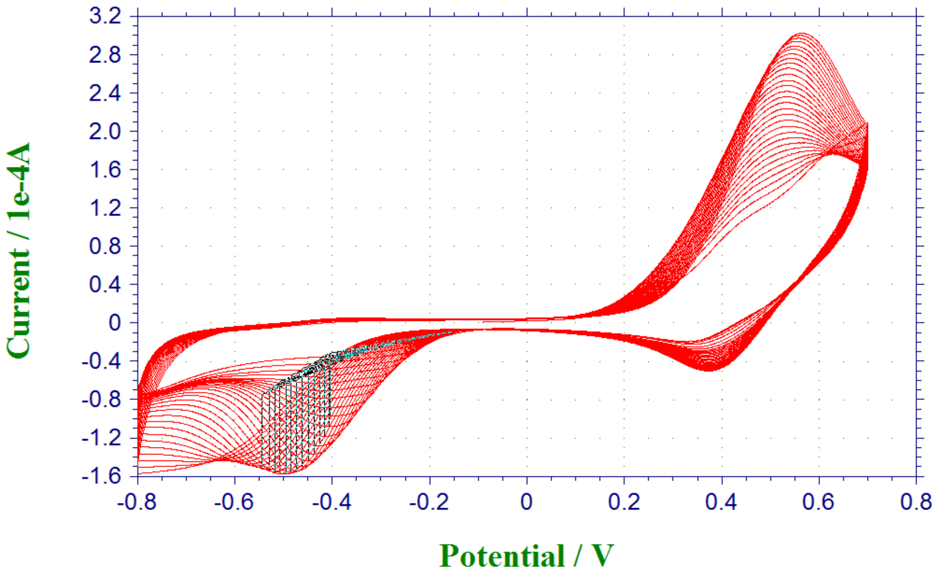

Figure 4. Repetitive scans of C1 (2mM) in 0.1 M Bu_4NClO_4–CH_2Cl_2 at SnO (from the1st to 25th cycles).

To analyse the constitutive elements, X-ray photoelectron spectroscopy (XPS) was conducted on W1. Figure 5(a) shows the survey scan subjected to W1 on ITO with ca. 112 nm thickness and the binding energies were summarised in Table 1. In Figure 5(b), two different nitrogen atoms present in W1 and were identified based on nitrogen peak fitting as shown in Figure 6. Peaks representing iminic nitrogen atoms were spotted at 399.2 eV [25], while peak representing the nitrogen atoms attached on the conjugated system was observed at 397.5 eV [26]. On the other hand, zinc $2p_{2/3}$ was observed at 1021.02 eV.

The presence of azobenzene linkage in W1 was confirmed by calculating and comparing the ratio between nitrogen 1s and zinc $2p_{2/3}$, N:Zn = 6:1 (found 1.5:6.5).

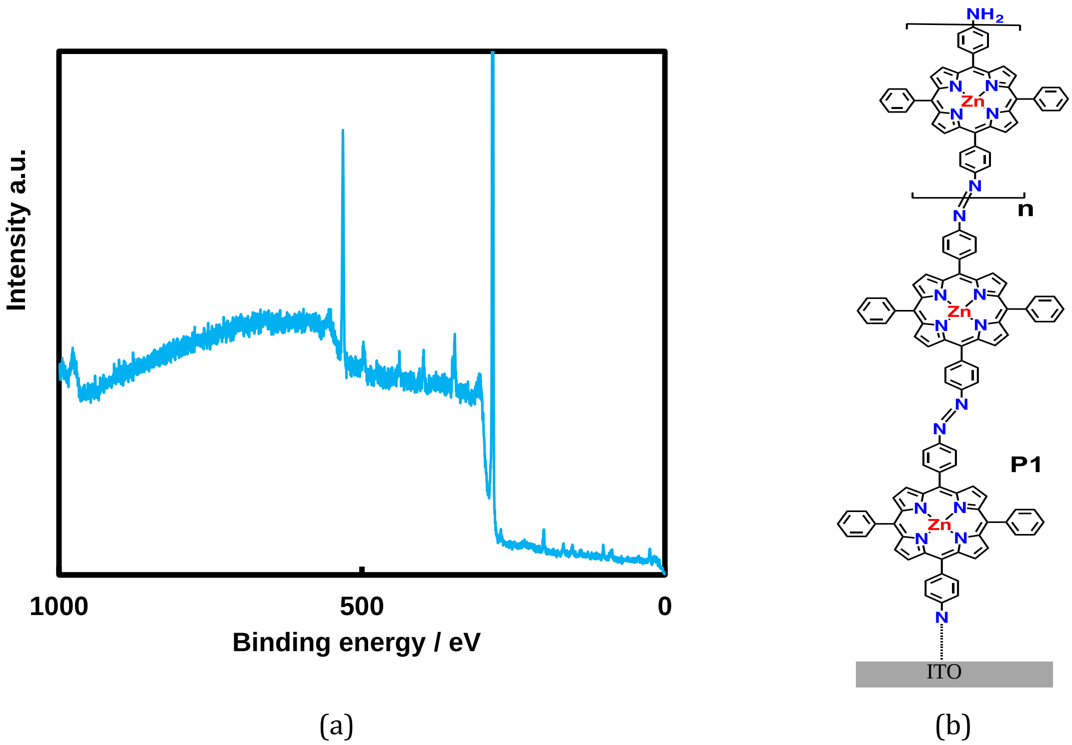

Figure 5. (a) Peak assignment for W1 on ITO based on survey scan and (b) Expected chemical structure with different N atoms in W1.

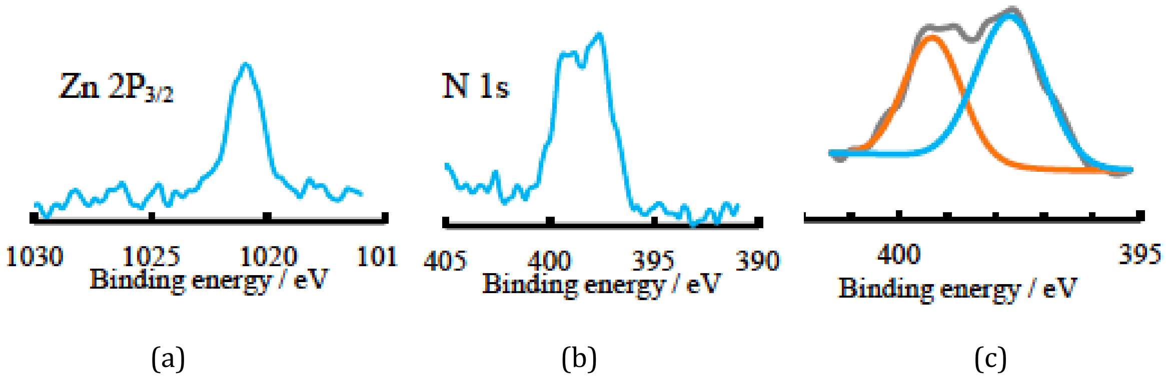

Figure 6. Narrow-scan XPS for W1, (a) Zn 2p3/2 region, (b) N 1s region, and (c) Deconvolution spectra of N 1s.

Table 1 Binding energies (eV) of elements in W1

Signal	Binding energy / eV
N 1s	399.2 , 398.0
Zn $2p_{3/2}$	1021.02
C 1s	283.9
O 1s	287.4, 531.2

When the light was irradiated (λ = 440 nm) onto W1, the photocurrent flowed through the electrolyte to ITO which resulted in a stable anodic photocurrent (Figure 7) and the photocurrent was ceased when the irradiation of light was cut off. Low quantum yield [13] for the photoelectric conversion might cause film defect at some part of modified ITO. Eventually, the size of the fluorocarbon O-ring directly affected the size of electrode active area. Therefore, some amount of photon absorbed might be lesser if the electrode active area included the defected part of modified ITO.

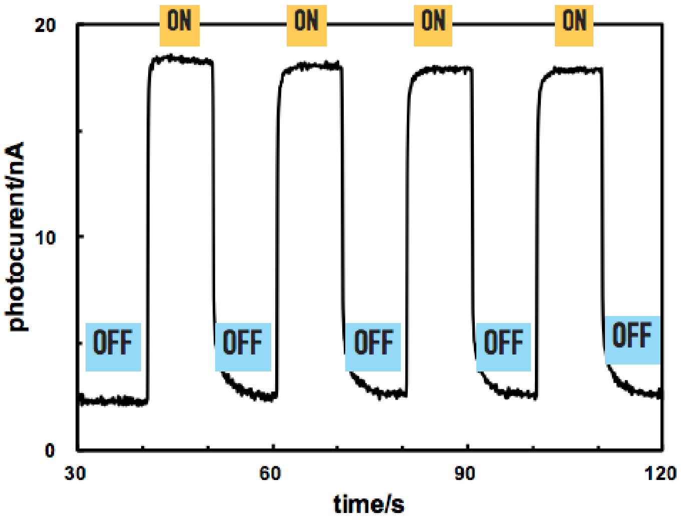

Figure 7. Generated anodic photocurrent upon light irradiation at 440 nm.

The position of HOMO and LUMO against ITO's Fermi level was relatively been modified by applying the bias voltage. Value of the LUMO level was obtained from absorption peak ($\lambda = 562$ nm) whilst the oxidation potential of modified ITO was determined by cyclic voltammetry. By referring to the electron transfer diagram (Figure 8), the electron in LUMO will be excited to HOMO and transmitted from W1 to ITO Fermi level from upon light irradiation to W1-modified ITO. An electron will be donated by TEOA which acts as a sacrificial reagent to hole in W1.

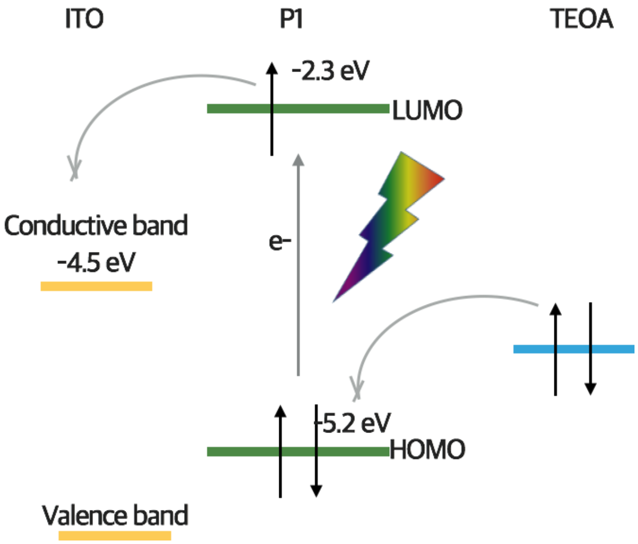

Figure 9. Schematic diagram of the plausible energy diagram of a modified ITO electrode, W1 and TEOA.

4. CONCLUSION

In conclusion, the microscopic measurement of W1 carried out by XPS disclosed the presence of azobenzene linkage in W1 and showed anodic photocurrent upon light irradiation. Good optical transparency of modified ITO is potential to be engaged in photonic devices, such as solar cells. On the other hand, research on next-generation energy storage, such as supercapacitor, is emerging in recent year. Therefore, a direct covalent modification GC surface is necessary for a high power system. Modified GC with redox-active materials will provide extra energy storage capacities and overcome problems, such as low charge storage capacities, compared to lithium batteries [27].

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