Journal of Materials and Manufacturing (2023) 2: 38-44

Journal of Materials and Manufacturing

Multi-walled carbon nanotubes and polypyrrole composites: A promising approach for dye-sensitized solar cell enhancement

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Abstract

The Dye-Sensitized Solar Cells (DSSCs) counter electrodes were fabricated using a three-electro deposition technique. The counter electrodes were constructed by depositing Polypyrrole (PPy) and its composites with multi-walled carbon nanotubes (MWCNTs) and copper layers on a stainless-steel substrate. This approach yielded 5-layer, 4-layer, and 2-layer MWCNTs/PPy/Cu composite counter electrodes. Electrochemical Impedance Spectroscopy (EIS), X-ray Diffraction (XRD), and Cyclic Voltammetry (CV) were employed to analyze the electrochemical properties, crystallographic structure, and electrocatalytic activity of the counter electrodes, respectively. The 5-layer MWCNTs/PPy/Cu-coated counter electrode demonstrated the lowest charge transfer resistance and exhibited superior catalytic activity compared to the other fabricated counter electrodes and the polypyrrole electrode.

Keywords: Solar cell, multi-walled carbon nanotubes, EIS, XRD, cyclic voltammetry.

1. Introduction

DSSCs have been attractive candidates for solar cells because they are easy to manufacture with inexpensive materials and have high energy conversion efficiency [1]. DSSCs usually consist of three main components: a counter electrode mainly consists of coated glass such as FTO (fluorine-doped tin oxide) with platinum film, an electrolyte containing redox species and dye-sensitized nanocrystalline TiO_2 (titanium dioxide) or ZnO (zinc oxide) [2]. Platinized counter electrodes are believed to have excellent conductivity and great catalytic activity for I_3- ions reduction [3]. Still, platinum has the problems of high cost, limited quantity on earth, and inconvenient transportation [4]. For this purpose, Pt can be replaced with excellent and cheap catalysts such as graphene, carbon black, conductive polymers like polyaniline, polypyrrole, poly(3,4-ethylene-dioxythiophene), and carbon nanotubes [5]. Carbon nanotubes (CNTs have excellent mechanical strength, large surface area, and rapid electron transfer ability [6, 7]. Multi-walled carbon nanotubes (MWCNTs) are very beneficial because they have properties of high electrocatalytic activity for I_3- reduction [8]. Furthermore, functionalized multi-walled carbon nanotubes (f-MWCNTs) can be easily dissolved in water, showing little toxicity and an environmentally friendly nature [9]. Conductive polymers are considered very

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DOI: 10.5281/zenodo.10401207
Received: 29 November 2023 / Accepted: 16 December 2023
ISSN: 2822-6054

suitable for making counter electrodes because they have great catalytic activity for I3- reduction, excellent stability, and are also affordable. Polypyrrole has great stability, easy processing, and comparatively excellent conductivity [10, 11]. Moreover, CNTs/PPy nanocomposites have excellent thermal stability and electrical and magnetic capacitive properties [12]. Additionally, metals such as copper show high corrosion resistance and excellent electrical and thermal conductivity [13, 14].

In this study, the fabrication of MWCNTs/PPy/Cu composite on stainless steel substrate as CE for DSSc using three electrode-electrodeposition methods is reported. This fabrication method is straightforward and cost-effective. The MWCNTs/PPy/Cu composite film shows excellent electrocatalytic and electrochemical properties for counter electrodes.

2. Material and Methods

2.1 Materials

MWCNTs (multi-walled carbon nanotubes) and polypyrrole were purchased from China, while copper sulphate was purchased from Sigma Aldrich.

2.2 Synthesis of MWCNTs

Acid-treated MWCNTs (multi-walled carbon nanotubes) were achieved by refluxing 60mg of MWCNTs in a 20ml (volume ratio 3:1) mixture of concentrated sulphuric acid (H_2SO_4) and nitric acid (HNO_3) at 60 º C for 1 hr. Functionalized MWCNTs were separated from an acidic mixture ($H_2SO4+HNO3$) using a centrifuge. The remaining solid was frequently washed with deionized water and vacuum dried at 110 º C for 6 hr. 100 ml aqueous solution consisting of 3 mg of f-MWCNTs, 0.05% of Ppy, and 0.5 M of H_2SO_4 was made. For a stable dispersion solution, this solution was mixed under ultra-sonication for 30 min. Using Princeton 263A electrochemical workstation, electrochemical synthesis of MWCNTs/Ppy/Cu composite film was performed in a three-electrode cell in which graphite electrode was used as a counter electrode, stainless steel with an exposed area of 1×1 cm^2 was used as working electrode and saturated calomel KCL (SCE) was used as a reference electrode. For the electrodeposition of MWCNTs/Ppy composite film on a stainless-steel substrate, the applied potential was set as 1-volt versus reference electrode for 300 sec. The electrodeposited composite film was washed out with deionized water. For the electrodeposition of copper on MWCNTs/Ppy composite film, a 100 ml aqueous solution of 0.5 M of H_2SO_4 and 0.01 M of $CuSO_4$ was made. The applied potential was set as 1 volt for 50 sec and then washed with deionized water. Similarly, Cu film and MWCNTs/Ppy composite film were electrodeposited layer by layer on a stainless-steel substrate for making 5 layers, 4 layers, and 2 layers of hybrid composite CEs. These CEs were dried at 60ºC for 3 hours in the oven.

3 Results and Discussions

3.1 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) was used to characterize the internal resistances of different CEs to analyze the influence of these CEs on DSSCs efficiency [15]. EIS characterization technique was used to explain the electrocatalytic activity of the CE for tri-iodide reduction reaction by determining the Rct (charge transfer resistance), which presents the electrocatalytic performance of the counter electrode [16, 17]. Typical impedance spectra of 5 layers, 4 layers, and 2 layers MWCNTs/Ppy/Cu hybrid composite deposited on stainless steel substrate as CEs are shown in Figure 1. Here Rs (series resistance) describes the resistance of the electrolytic resistance, and the two identical electrodes and high-frequency intercept on the real axis represent the series resistance. For tri-iodide reduction at the electrolyte/CE interface, the low and high-frequency range at the semicircles step are assigned to the impedance as Rct (charge transfer resistance).

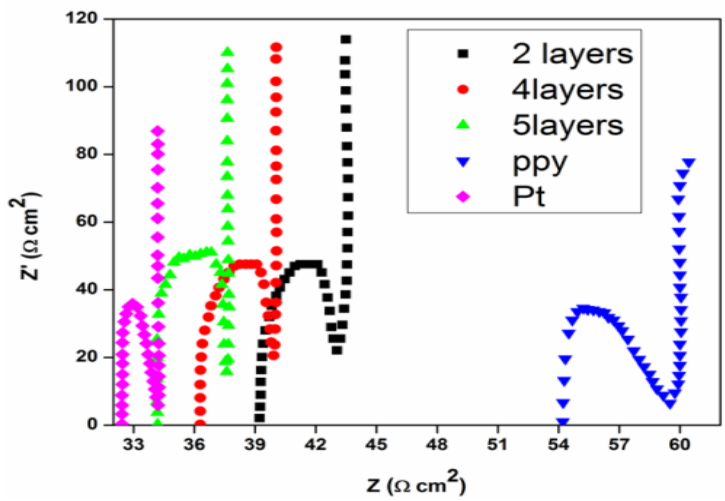

Fig. 1. Typical Impedance Spectra for Pt, Ppy, and different layered MWCNTs/Ppy/Cu composite

Table 1, Clearly represents the resultant impedance parameters calculated from EIS spectra. It is seen from Table 1 that Rs(series resistance) of the CE for Polypyrrole is 54.2Ω, 2 layers MWCNTs/Ppy/Cu composite is 39.2Ω, 4 layers MWCNTs/Ppy/Cu composite is 36.3Ω,5 layers MWCNTs/Ppy/Cu composite is 34.1Ω and for Pt is 32.4Ω. All these results had nearly similar values, which indicated that all the counter electrodes were firmly bonded to the stainless steel substrate. Charge transfer resistance (Rct) of the MWCNTs/Ppy/Cu composite CEs has minimal values than polypyrrole CE. Plots show qualitatively that the Rct of a cell increased in the sequence as Pt film< 5 layers composite<4 layers composite<2 layers composite <Ppy film.

Table 1. EIS parameters calculated for different CEs

CEs	Rs(Ω cm^2)	Rct (Ω cm^2)
PPy	54.2	5.3
2 layers MWCNTs/PPy/Cu composite	39.2	3.8
4 layers MWCNTs/PPy/Cu composite	36.3	3.6
5 layers MWCNTs/PPy/Cu composite	34.1	3.5
Pt	32.4	1.8

This indicates that polypyrrole CE has a poor electrocatalytic activity for tri-iodide ion reduction; however, composite film of MWCNTs/Ppy/Cu efficiently caused the reduction of tri-iodide to I- in the electrolyte, which indicates the porous structure of polypyrrole film and high surface area of MWCNTs and this improves the electrocatalytic activity of the CE Smallest Rct (charge transfer resistance) of the hybrid composite (MWCNTs/Ppy/Cu) cell correlated well with the highest Jsc value of the relevant DSSC.

3.2 XRD Analysis

X-ray diffraction (XRD) was used to characterize the structure and identity of the test samples. Fig presents the typical x-ray diffractogram of the test samples such as Ppy film, 5 layers MWCNTs/PPy/Cu composite, 4 layers MWCNTs/Ppy/Cu composite, 2 layers MWCNTs/Ppy/Cu composite in which XRD peaks at 44.05º and 25.8º were indexed to (100) and (002) showed the reflections of multi-walled carbon nanotubes (MWCNTs) [18] . At 21.1º, broad diffraction peaks showed the MWCNTs/Ppy composite film, which can be

referred to as the influence of the polymer group of polypyrrole [19]. The composite film consisting of MWCNTs/Ppy not only has a broad peak focussed at 21.1º, but all the sharp, clear peaks of MWCNTs showed the existence of MWCNTs distributed in Ppy nanoparticles, as shown in Figure 2.

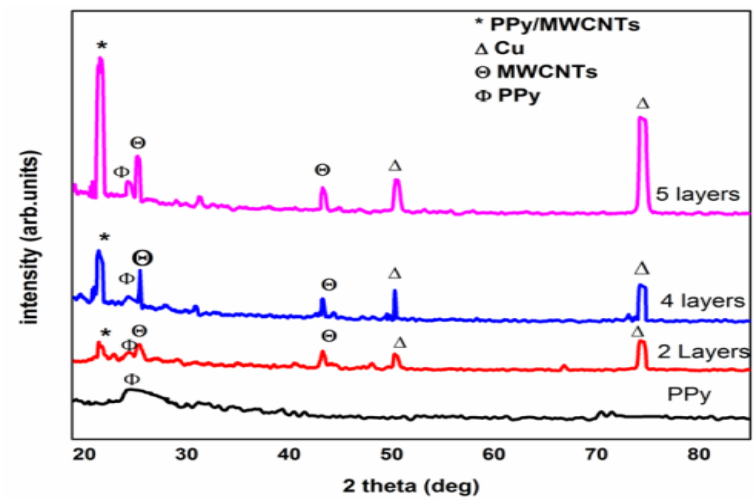

Fig. 2. XRD patterns for Ppy, different layered MWCNTs/Ppy/Cu composite

Typical XRD peaks at 50.4º and 74.1º present the metallic copper (Cu). These clear peaks indicate the structure of metallic copper (Cu) as face-centered cubic (Fcc) in MWCNTs/Ppy/Cu composite film. XRD pattern at 24º shows a hump, which is mainly for conducting amorphous Polypyrrole (Ppy) [20], and the complete XRD pattern without any particular peak indicates that polypyrrole has an amorphous structure [21]. The amorphous nature of Ppy is beneficial for CE because the electrolyte can efficiently enter the bulk of the electrode, and the complete surface area of the electrode can be used for electrocatalytic activity [22].

3.3 Cyclic Voltammetry

The Cyclic Voltammetry technique is applied to different electrodes because it analyses the relationship between an electrochemical cell's reaction kinetics and ion diffusivity. In the DSSC system, usually, electrons were inserted into the photo-oxidized dye from electrolyte's I- ions for $3I_2 + 2e- \rightarrow 2I_3-$ and then the generated I3- ions were reduced on the counter electrode for $I_3- + 2e- \rightarrow 3I-$. Figure 3 shows the cyclic voltammetry curves of Ppy film, 2 layers MWCNTs/Ppy/Cu composite film, 4 layers MWCNTs/Ppy/Cu composite film, 5 layers MWCNTs/Ppy/Cu composite film and Pt film CEs in the potential range from -1.2 to 1.2 V taken at a scan rate of 5 for I- /I_3- redox system. Each curve in Figure 3 presents two sets of redox waves. The relative positive set is associated with the reaction of I_2 /I_3-, and the negative set is assigned to the redox reaction of I_3- /I.

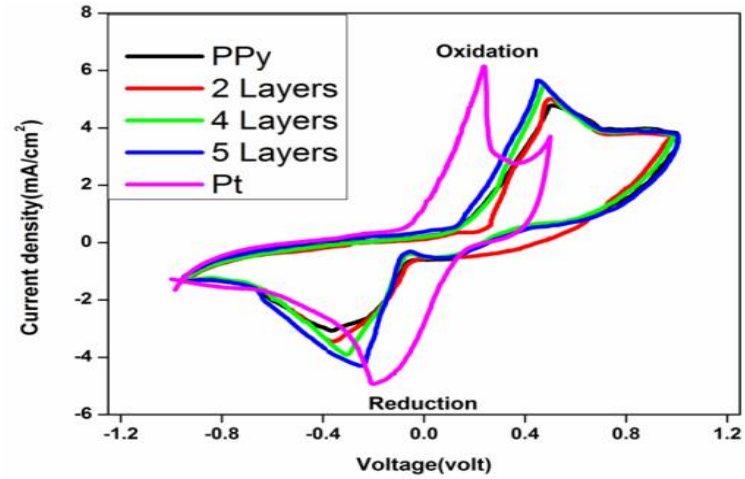

Fig. 3. CV curves for Pt, Ppy, different layered MWCNTs/Ppy/Cu composite

Figure 3 gave nearly identical shapes of redox peaks for polypyrrole film CE, Pt film CE, and different layered MWCNTs/Ppy/Cu composite CE in I- /I3- redox system, but 5 layers composite CE exhibits more positive cathodic-peak potential and higher cathodic peak current density (-0.24 v, 4.0mA/cm^2) than polypyrrole CE (-0.36v, 2.4mA/cm^2), 2 layers composite CE (-0.35v, 2.9mA/cm^2) and 4 layers composite CE (-0.30v, 3.5mA/cm^2) as shown in Table 2. This revealed that for I_3- to I- reduction, 5 layer composite possessed superior conductivity and much smaller overpotential, indicating the property of a larger active surface area. As multi-walled carbon nanotubes have excellent conductivity, so by increasing the quantity of MWCNTs with different layers electrodeposition method, the absolute value of cathodic peak potential (Vpc) decreases and the absolute value of cathodic peak current (Ipc) increases [23].

Table 2. CV measurement for different CEs

CEs	Ipc	Epc
PPy	2.4	-0.36
2 layers MWCNTs/PPy/Cu	2.9	-0.35
4 layers MWCNTs/PPy/Cu	3.5	-0.30
5 layers MWCNTs/PPy/Cu	4.0	-0.24
Pt	4.4	-0.20

A sequence of the current density of different counter electrodes coincides well with the charge transfer resistance (Rct) calculated from the EIS (electrochemical Impedance spectroscopy) test. This is because of the porous structure of Ppy, which allows rapid electron transfer from Cu (copper) and also provides a larger contact area with electrolyte. It can also be considered that Cu(copper) nanoparticles have a higher surface-to-volume ratio, which gives a larger interfacial surface area on highly porous Ppy associated with redox I_3-/I-electrolyte. Notably, 5 layers MWCNTs/Ppy/Cu CE showed the lowest Vpc and highest Ipc which is nearly comparable to Pt CE.

4. Conclusion

Three different layered such as 5 layers MWCNTs/Ppy/Cu composite, 4 layers MWCNTs/Ppy/Cu composite and 2 layers MWCNTs/Ppy/Cu composite CEs were fabricated by using the three-electrodeposition method and their impedance and electrocatalytic activity was analyzed to improve the power conversion efficiency of a dye-sensitized solar cell. Cyclic voltammetry and electrochemical impedance spectroscopy present the electrochemical analysis of different layered MWCNTs/Ppy/Cu composite CEs. It was found from this characterization analysis that when we increase the deposition layers of composite films on stainless steel substrate, then Rct (charge transfer resistance) at the interface between CE and electrolyte decreases and cathodic current density increases and hence electrocatalytic activity for I-/ I3- redox couple increases. So it can be concluded from this present research that excellent photoelectric properties, easy fabrication methods, and inexpensive costs allow MWCNTs/Ppy/Cu composite electrodes to be a reliable alternative to Pt used in dye-sensitized solar cells.

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