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Effect of Thickness in Carbon Nanotube Electrode Layer for Electrochemi-Luminescence Cells Applications

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Abstract – The nanoelectrode layer in electrochemi-luminescence (ECL) cells can be improved the performance of light intensity. In this work, the ECL cells were fabricated using carbon nanotubes (CNT) and Ru(II) complex as a luminescent material. We reported to the effect of the thickness of the CNTs layer in ECL cell. The produced ECL cell consists of F-doped SnO_2 (FTO) glass/Ru(II)/ thickness of CNTs/FTO glass. At 3.5 V, the measured highest current and highest luminance of CNTs-based on ECL cells was 48 mA and 15.02 cd/m^2 at CNT-5 μm. The maximum of ECL efficiencies was 0.00893 lm/W for CNT-5 μm. When, the applied voltage increases at 4-5 V is causing to maximum ECL efficiency for CNTs-based on ECL cell. The peak intensity of thickness of CNTs-based on ECL cell was ~620 nm of CNTs and ~625 nm of without CNT, which is a similar color and responded dark orange color, were not affected to the added electrode material. The ECL cell with CNTs showed optimum for light emission was the thickness of CNT-5 μm electrode. The use of CNTs-based on ECL cell significantly improves the ECL efficiency and long-term stability.

Keywords: Electrochemi-luminescence (ECL) cells, Carbon nanotube, Ru(II) complex

1. Introduction

Currently, the nanostructure electrode layer widely used in the applications such as a chemical sensor (biosensor), dye-sensitized solar cells (DSSCs), and electrochemi-luminescence (ECL) cells. It can be stimulated electron transfer between surface electrodes to material layer increased [1-4]. The ECL cell devices are well known in the light-emitting phenomenon which composed of two electrodes with the transparent conducting oxide (TCO) and luminescent material with Ru(II) complex layer [2, 5-7]. The researchers are interested in the ECL cell devices due to it is simple structure devices. Therefore, the efficiency of ECL cell device is based on the electrode layer that structure electrode is nanostructure electrode. The application of nanostructure electrode is used, metal oxide nano-electrode and one-dimensional structure such as nanoparticles, nanowires, nanotubes, and nanorods. The carbon nanotubes (CNTs) are an alternative that can be applied in ECL cells. It is a semiconductor which can be applied to the electrode of ECL cell.

The nanostructure of CNTs is one-dimensional systems, a synthetic material that gets the most attention. CNTs have a special structure that is different from the three allotropes (diamond, graphite, and buckminsterfullerene). CNTs are formed from carbon atoms arranged in a sheet, which has a high fluidity (Similar to the structure of graphite). The carbon atoms are coherence into a lattice with hexagonal holes, which is a pipe or a tube [8]. CNTs are very small tubes at the nanometer scale, which has a diameter of tubes in the range of 0.4 to 4.0 nm. It can be a synthesized structure with a length of up to 10 μm. CNTs can be synthesized by two types; a single wall carbon nanotube (SWCNT) and a multi-wall carbon nanotube (MWCNT) which have band gaps ~0.5 eV at diameter 1.5 nm [9-11]. The electrical properties of CNTs are semiconductor or superconductor which is based on the synthesis of carbon atoms arranged along the wall of the tube. All properties of CNTs may be applied to the electrode layer in the ECL cell. Often, the research reported in the thickness of the electrode layer which have affected to electrical and optical properties of the ECL cell [12, 13]. Thus, we are focusing on optimum of the thickness of the CNTs electrode layer on an ECL cell device which may be increased the oxidation and reduction reaction of Ru(II) complex and recombination between Ru(I) and Ru(III) thus the overall conversion efficiency can increase.

In this paper, we present an optimum thickness of CNTs-based ECL cell. In order to, the increased area electrode are the interface between CNTs electrode and Ru(II) complex in the cell. The CNTs have semiconductor can be received density of electrons on the surface CNTs electrode with Ru(II) complex. The ECL cell with CNTs was fabricated layers nanostructure via F-doped SnO_2 (FTO) glass / Ru(II) / CNTs / FTO glass. The electrical and optical properties of the CNTs electrode layer of the ECL cell are investigated by each thickness of the CNT layer which is suitable for the ECL device.

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2. Experimental Setup

The structure used CNTs electrode for ECL cell device, show in Fig. 1. The thickness of the electrodes between FTO glass is approximately 60 μm, which was injected with $Ru(bpy)_3^{2+}$. The reason of using FTO glass instead of ITO is because of the excellent heat resistance that eliminates further problems. The CNTs layer with 1-7 μm of thicknesses are connected in 3-D structure with $Ru(bpy)_3^{2+}$. The coated CNTs can be enhanced $Ru(bpy)_3^{2+}$ in the cell because of the surface of CNTs was increased. Thus, the large surface area became very conductive, its can the fast transfer of more electric charges in $Ru(bpy)_3^{2+}$ molecules [14, 15].

The CNTs synthesis has been grown by spin-coating technique can be discussed elsewhere [16]. The CNTs paste solution was fabricated CNTs (muti-wall nanotube: MWNT; Hanwha Nanotech) powder and sodium dodecyl benzene sulfonate (SDBS; CHEMMAX) by mixing in the ratio 20 mg: 20 mg, and the deionized water of 20 ml for the surfactant, stirred 10 minutes. The dispersion of CNTs was prepared by bath sonicator (Branson, 2510) for 5 min and bar sonicator (Sonics & material, VCX500) for 20 minutes [16-18]. The process of CNTs can be shown Fig. 2.

The synthesis of ECL cell device was used Tris(bipy ridine)ruthenium(II) chloride ($Ru(bpy)_3Cl_2$; SIGMA-Aldrich) and ammonium hexafluorophosphate (NH_4PF_6; WAKO) and propylene carbonate (PC; SIGMA-Aldrich). $Ru(bpy)_3Cl_2$ and NH_4PF_6 (0.5g: 0.5g) were dissolved in the distilled water, and stirring process of the solution for 1 h.

The both solutions results in the formation $Ru(bpy)_3(FP_6)_2$.

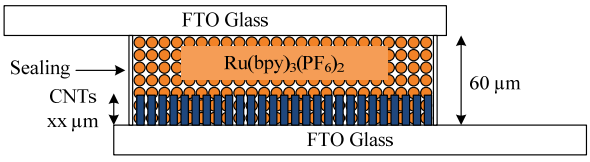

Fig. 1. The schematic of ECL cell with CNTs

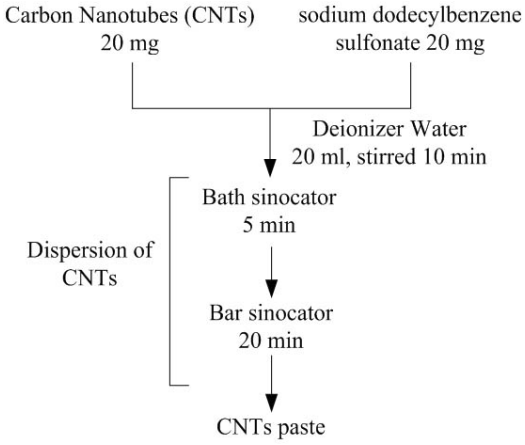

Fig. 2. The process of CNTs paste

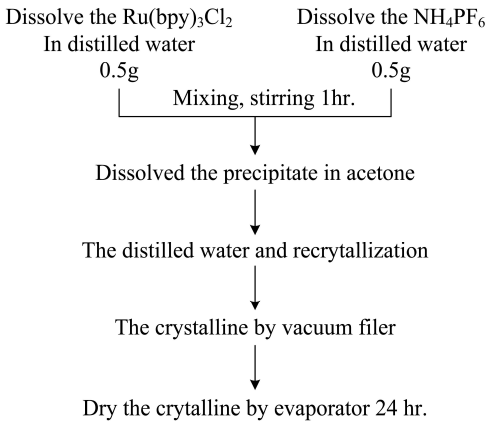

Fig. 3. The process of $Ru(bpy)_3(FP_6)_2$.

The precipitate of $Ru(bpy)_3(FP_6)_2$ was dissolved in the acetone. The precipitates were collected from recrystallization via distilled water. After that, the crystalline collected by and dried under vacuum for 24 h [7]. The $Ru(bpy)_3(FP_6)_2$ powder and PC solution ratio are achieved at 0.04g : 0.448g for [19-20]. Fig. 3 shows the process of $Ru(bpy)_3(FP_6)_2$.

For fabrications of a CNTs-based ECL cell, FTO glass with size an area 2×3 cm^2 was washed by ultrasonic (JAC 4020) and dried at 120 °C [7]. A layer of CNTs was coated on the FTO glass by a spin coater (ACE-1020 Series) in the area of 1×1 cm^2, followed by annealing at 450°C for 30 min. The coated CNTs on FTO glass was operated at thickness 1, 3, 5 and 7 μm. The two electrodes were sealed by polymer spacers (Himilian; DuPont-Mitsui Polychemicals, thickness 60 μm). The Ru(II) solution of 0.16 M with PC was injected into the gap between two electrodes [1, 19].

The ECL cell using CNTs electrode was measuring luminescence intensity and the current-voltage characteristics. All characteristics were measured using a spectroradiometer (Konica Minolta, CS-2000), an arbitrary waveform generator (Agilent, 33250A), and a digital storage oscilloscope (HAMAG, HMO1024).

3. Experimental Results

In this paper, ECL cell using CNTs electrode measurement are to be divided by its physical characteristics, electrical properties, and optical properties, also to find more suitable of the thickness of the CNTs electrode for ECL device. In physical characteristic side, is to analyze the crystallization at both of the structure surfaces.

Fig. 4 (a) and (b) are shown photographs of CNTs and annealing CNTs paste coated on FTO glass. In Fig. 4(a) is show the product of CNT, which made from the process the CNT solution in Fig. 2. The CNTs paste coated on FTO glass using by spin coater in area 1×1 cm^2, (right) and annealing at 450°C (left), can show in Fig. 4(b). The SEM

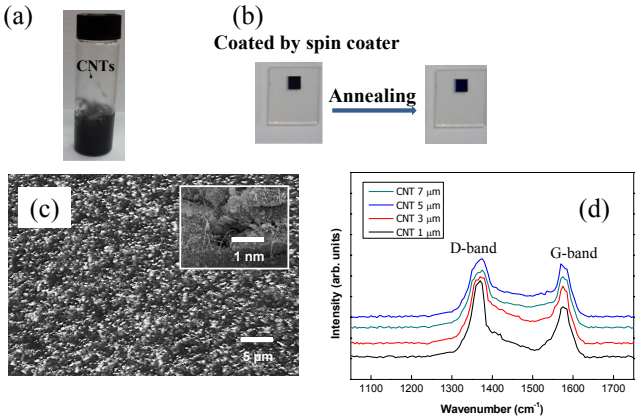

Fig. 4. Characterization of CNTs paste (a) Photograph of a vial of CNTs (b) Photograph of coating and paste. (c) SEM image of the CNT thickness-5μm coated on an FTO glass. (d) Raman spectrum of the CNTs

image of CNTs at 5 μm of thickness was measured by scanning electron microscopy (SEM, Hitachi S-3000H), can show Fig. 4(c). It resembles the shape of a growing tube, show in Fig. 4(c) inset. There is an array scattered on the surface. The mass and the surfactant of CNTs were 0.45-0.48 mg and a CNT density of 0.23-0.25 mg/cm^2. The quality of the CNTs was measured by MultiRAM FT-Raman spectrometer (Bruker, Raman ScopeIII). The peak intensity of CNTs was showed by Raman spectroscopy (Fig. 4(d)). The specific surface area of the CNTs investigated by the Brunauer-Emmett-Teller (BET) method was ~454.2 m^2 /g.

The ECL cell represents the electrode material, thus the sample thickness of CNT electrode and ECL without CNTs electrode have the following configurations: FTO glass / Ru(II) / CNT(thickness-1 μm) / FTO glass, FTO glass / Ru(II) / CNT(thickness-3 μm) / FTO glass, FTO glass / Ru(II) / CNT(thickness-5 μm) / FTO glass, FTO glass / Ru(II) / CNTs(thickness-7 μm) / FTO glass and FTO glass / Ru(II) / FTO glass, respectively.

The intensity distributions of the thickness of CNTs for ECL cells are shown in Fig. 5. The peak intensity was ~625 nm of without CNT and 620 nm of CNTs-based ECL cell, which is very similar, is almost no effect on all electrodes. All electrodes of the ECL cells were showed responds dark orange emission of the ECL cell, and confirmed not to influence ECL device's luminous color. The peak intensity of CNT-7 μm less than that CNT-5 μm due to the collision of electrons and Ru(II)$^+$ (mean free path) in the CNT causing light intensity was decreased.

For the electrical properties, the sheet resistance of CNTs electrode was 8.45 Ω/sq of CNT-1 μm, 8.95 Ω/sq of CNT-3 μm, 9.25 Ω/sq of CNT-5 μm and 9.46 Ω/sq of CNT-7 μm. The applied voltage and frequency on cells are 0-5 V and 60 Hz for tested. The output current of CNTs-based on ECL cells were 28 mA for CNT-1 μm, 37 mA for CNT-3 μm, 48 mA for CNT-5 μm, 46 mA for CNT-7 μm and 21

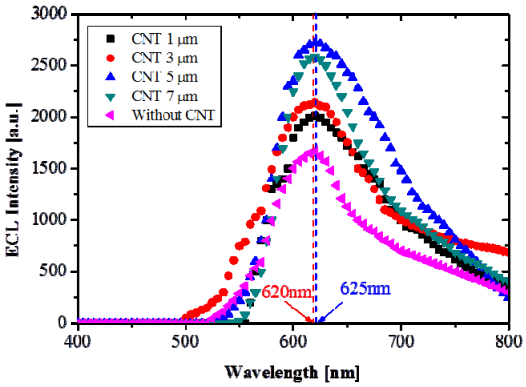

Fig. 5. The intensity distribution of ECL cell with thickness of CNT 1 μm, CNT 3 μm, CNT 5 μm, CNT 7 μm and without CNT

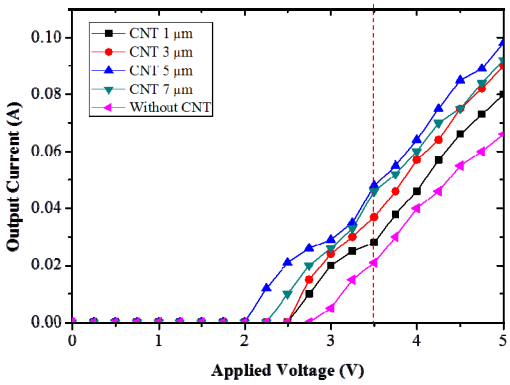

Fig. 6. The I-V curve of thickness of CNTs-based on ECL cell at CNT 1 μm, CNT 3 μm, CNT 5 μm, CNT 7 μm and without CNT

mA for without CNT at 3.5 V 60 Hz, show in Fig. 6. The current of CNT-5 μm was more than these CNTs and without CNT due to the large area surface on CNT reflected electrons in reducing reaction with $Ru(bpy)_3^{2+}$.

Fig. 7 shows the relationship between luminance and the thickness of CNTs-based on ECL cell. The applied voltage was 0-5 V, the frequency is 60 Hz.

Here nanotubes represent a cell with CNTs of thickness at 1, 3, 5 and 7 μm, respectively. The threshold voltage of the light emission start was 2.25 V for CNT-5 μm, which was lower than 2.75 V for CNTs 1 μm and 3 μm, 2.5 V for CNTs 7 μm and 3 V for the cell without CNTs. In addition, the threshold voltage decreases with increasing the thickness of CNTs-based on ECL cells.

This result shows the decrease of the threshold voltage is related with the CNTs structure. The luminance of thickness of CNTs-based on ECL cell were 7.21 cd/m^2 for CNT-1 μm, 10.11 cd/m^2 for CNT-3 μm, 15.02 cd/m^2 for CNT-5 μm, 13.21 cd/m^2 for CNT-7 μm and 5.05 cd/m^2 for without CNT at 3.5 V 60 Hz. The CNT-5 μm was maximum luminance because the large surface area of the CNTs would be responsible for the higher output current and electrons can diffuse in the CNTs [15, 17].

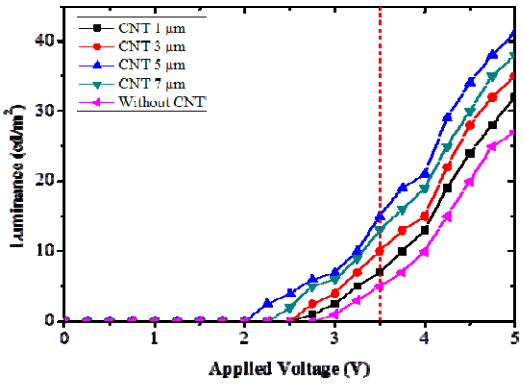

Fig. 7. The luminance of thickness of CNTs-based on ECL cell at CNT 1 μm, CNT 3 μm, CNT 5 μm, CNT 7 μm and without CNT

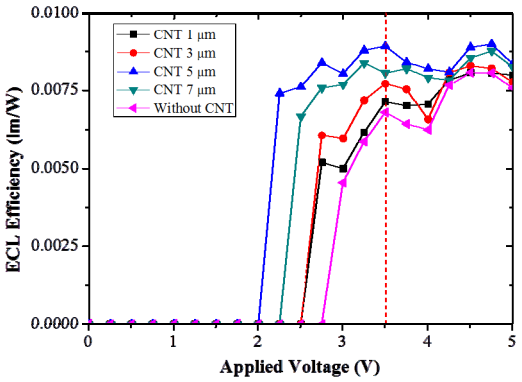

Fig. 8. The ECL efficiency of CNTs-based on ECL cell at CNT 1 μm, CNT 3 μm, CNT 5 μm, CNT 7 μm and without CNT.

The efficiency of ECL cell can calculate from light intensity per electrical power (lm/W), the following equation: [7, 21]

$$Eff_{ECL} = \frac{I_V \cdot A_{surf}}{V \cdot I_{out}}, \quad (1)$$

when I_V is intensity (cd/m^2) and A_{surf} is emission surface (m^2). At 3.5V, the efficiencies were 0.00714 lm/W for CNT-1 μm, 0.00772 lm/W for CNT-3 μm, 0.00893 lm/W for CNT-5 μm, 0.00807 lm/W for CNT-7 μm and 0.0068 lm/W for without CNT, show in Fig. 8. The maximum of ECL efficiency was in the 4-5 V. The applied voltage increases causing the ECL efficiency were decreased due to the luminance and current are small increase make for efficiency is decreased followed reports [7, 19].

4. Conclusion

This paper presents the results of electrode material used by CNTs electrodes in ECL cell device. The performance of ECL cell with the nano-electrode material was CNTs for light emission. The thickness of CNT-5 μm has been light-emitting more than cell other CNTs and without CNTs electrodes. The threshold voltage of light emission starts of CNT-5 μm was lower than other CNTs, and 3 V for the cell without CNTs. The maximum output current was 48 mA for CNT-5 μm (At 3.5 V), which more than cells other thickness of CNTs and without CNT electrodes. The applied voltage maximum ECL efficiencies of CNTs were 4-5 V. The voltage increases, causing the ECL efficiencies of the thickness of CNTs are decreasing. The peak intensity of CNTs-based on ECL cell was ~625 nm of without CNT and ~620 nm of CNTs-based ECL cell, which is very similar for color, have been responded dark orange color which was not influenced by the change in electrode material. The ECL cell with CNTs showed optimum for light emission was more than 5% for comparable other CNTs and ECL without CNT electrodes. The CNTs electrode can be improved light emission performance of ECL cell.

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