Synthesis and properties of platinum on multiwall carbon nanotube modified by chitosan

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Abstract. Platinum nanoparticles on multiwall carbon nanotubes (Pt/MWCNT) play an important role in fuel cell to convert the chemical energy from a fuel into electricity. In this study, Pt/MWCNT electrocatalysts were prepared by chemical reduction of the metal salts in chitosan as the support. Firstly, commercial MWCNTs were functionalized by oxidative process using a mixture of nitric acid and sulfuric acid. Then, functionalized MWCNTs were mixed with chitosan-acetic acid solution to conduct grafting reaction with NH$_2$ groups in chitosan by solution polymerization method. Platinum nanoparticles were loaded onto the surface of the MWCNTs after hexachloroplatinic acid was reduced by sodium hydroxide solution. The result showed that Pt was attached on MWCNT based on analysis from EDS, XRD, and UV Vis Spectroscopy. UV Vis analysis indicates the plasmon absorbance band of Pt nanoparticles in Pt/MWCNT, while XRD analysis confirmed the size of Pt particle in nanometer. This elucidates the potential procedure to synthesize Pt/MWCNT using chitosan.

1. Introduction

Platinum (Pt) as catalyst in fuel cell devices has a significant influence in the process of converting chemical energy into electricity. However, since platinum prices are quite expensive [1] and the inherent lack of stability of Pt when supported on carbon-black (Pt/C) [2], the reduction of Pt is required by making platinum on a nanometer scale. This makes platinum require catalyst support that can help increase platinum capacity and utilization [3, 4] A suitable support for an electrocatalyst should possess high surface area, good electrical properties, and high electrochemical stability under PEM Fuel Cell operating conditions [5]. Carbon Nanotubes (CNTs) potentially match these requirements since it has high surface area, high platinum dispersion, and smaller particle size, so it can reduce production costs by reducing platinum use [6].

To improve the catalytic activity of the platinum catalysts, many polymers have been used as support for metal nanoparticles, such as nafion, polyaniline, and chitosan [7]. Chitosan is a polymer derived from shrimp and crab shells waste that has cation polyelectrolyte properties so it can bind to metal [8]. The amine and two hydroxyl groups on each glucosamine monomer act as adsorption sites, especially the amine groups which are strongly reactive with metal ion [9]. Honda Wu [10] had been using chitosan to modify CNTs by solution polymerization method that adsorption of platinum was better for carbon nanotube modified by chitosan. The oxidation performance for carbon nanotube grafted by chitosan trigger the chelation reaction between chitosan and platinum ion [10]. Another
study reported preparation of Pt, Fe and Co nanoparticles by chemical reduction of the metal salts in chitosan as support [7].

In this study, we report a novel process to synthesize Pt/MWCNT by modifying functionalized CNT with chitosan that conducted at ‘mild’ condition. The presence of Pt in Pt/MWCNT was carried out using UV-Vis spectroscopy analysis. Chemical composition and crystallographic structure of the obtained Pt/MWCNT will be confirmed by energy dispersive X-ray spectroscopy (EDS) and by X-ray diffraction (XRD) measurements.

2. Materials and method

2.1. Materials and chemicals

The MWCNTs were purchased from He Ji Company (95% purity, outer diameter 8-15 nm, Hongkong). The MWCNTs were firstly functionalized by surface oxidation method using a mixture of nitric acid and sulfuric acid as previous procedure [11]. Chitosan was obtained from local industry in Bogor, West Java. Chloroplatinic acid hexahydrate (H₂PtCl₆.6H₂O) was purchased from Sigma-Aldrich Company and was used as received. Nafion solution 5% was purchased from Fuelcell Earth. All other chemicals such as sulphuric acid, nitric acid, acetic acid glacial, sodium hydroxide, 2-propanol, and ethanol were purchased from Merck and used without further purification. Deionized water was used in all aqueous solutions and rinsing procedures.

2.2. Preparation of Pt/MWCNT electrocatalyst

The preparation of Pt/MWCNT electrocatalyst has been done according to the following procedures. A quantity of 100 mg of functionalized MWCNTs were dispersed in 20 mL of chitosan solution (1 g of chitosan was dissolved in 100 mL of 2% (v/v) acetic acid solution), followed by 1 h of sonication to achieve good dispersion. Afterward, the transparent yellow solution of H₂PtCl₆.6H₂O/etanol (15 mL, 0.007 M) was added slowly into the mixture of MWCNT-chitosan at the rate of 5 s/drop under stirring condition of 450 rpm. This solution was then stirred for 1 h. Subsequently, NaOH solution (2 M) as the reducing agent was added drop-wise into the mixture to increase the pH value until it reached 11.5. The reduction process of Pt precursors into Pt nanoparticles was carried out by refluxing the mixture under ‘mild’ condition, i.e. at 80 °C for 1 h and then cooled down to room temperature. The obtained material was filtered and washed with deionized water several times until neutral condition was achieved and finally dried in the vacuum oven at 40 °C.

2.3 Characterizations

Samples for transmission electron microscopy (TEM) were prepared by dispersing powder in ethanol, placing it in an ultrasonic bath, then putting droplets onto the grids and drying it in air at room temperature. TEM images were recorded using a FEI Tecnai G2 20 S-Twin operated at 200 kV. The surface morphology and elemental identification of the samples were characterized by Scanning Electron Microscope (SEM) equipped with EDS (Hitachi SU3500) under operating voltage of 20 kV. The crystal structure of the Pt nanoparticles supported on MWCNTs was determined by powder XRD (Shimadzu XRD-7000) with CuKα radiation. The average crystallite size of the Pt particles in the catalyst powder was calculated from full width at half maximum (FWHM) values using Debye-Scherrer equation [12]. For UV Visible characterization, a mixture of nafion solution and 2-propanol was used for dispersing Pt/MWCNT, while f-MWCNT and H₂PtCl₆ were dispersed in ethanol. About 20 mL of 2-propanol/nafion solution (ratio of 35:65) was mixed with 0.001 g of Pt/MWCNT and dispersed using ultrasonic bath for 3 h. UV-visible absorption spectra were recorded by spectrophotometer HITACHI U-2800 operated between 200 up to 300 nm at a scan speed of 100 nm/min.
3. Results and discussion

It is well known that functionalization of CNT by oxidised acid (acidic mixture of nitric acid and sulphuric acid) destroy and shorten the CNT to small segments by the breakage of the chain [6]. Figure 1 shows TEM images of MWCNT before and after oxidized treatment. The arrows in figure 1b serves as evidence that the outer walls of the functionalized MWCNT has been destroyed, which leads to the breakdown of the C-C bond in the CNT backbones. However, oxidized treatment of MWCNT also introduces some new functional groups, such as hydroxyl and carboxylic groups, which are formed on the MWCNT surfaces. Figure 2 illustrates our concept on synthesis method of Pt/MWCNT modified by chitosan. Introduction of chitosan into the functionalized MWCNT creates link between amine groups and some part of carboxylic groups. The reduction process was completed by adding NaOH solution to reduce Pt\(^{2+}\) into Pt (IV) metal nanoparticles. In this reaction, deposition of Pt nanoparticles on the surface of MWCNT occurred through amine groups and carboxylic groups.

![Figure 1. TEM images of MWCNT (a) before, (b) after surface oxidized treatment.](image)

![Figure 2. A schematic diagram of synthesis of Pt/MWCNT modified chitosan.](image)

The XRD pattern of Pt/MWCNTs is shown in figure 3. The diffraction peaks in the XRD pattern indicate good crystallinity of the supported nanoparticles. The peak at \(\sim 26^\circ\) is attributed to graphite crystallographic planes (002) of MWCNT. Pt/MWCNT shows the presence of diffraction peaks at nearly 40°, 46°, 68°, and 82° corresponding to (111), (200), (220), and (311) planes of platinum, respectively. These are analogous to the face-centered cubic (fcc) structure of the noble metal. The average crystallite size of platinum calculated from the Debye-Scherrer equation is less than 10 nm, which proves that Pt is nanoparticles.
SEM images and elemental analysis using EDS are shown in figures 4 and 5, respectively. It can be seen that Pt nanoparticles have been successfully deposited on the surface of MWCNT. The Pt phase appearance is convincingly confirmed by EDS analysis (figure 5b). Besides C and Pt signals, EDS spectrum includes also signals connected with O, Cl, and Ca elements. The peak of O element is connected with the functionalization process of CNTs, while the peaks of Cl and Ca element are connected with the presence of remained catalysts impurities. Cl signal suggested that H$_2$PtCl$_6$ was not reduced completely to Pt by NaOH.

**Figure 4.** SEM images of the (a) surface oxidised MWCNT and (b) Pt/MWCNT-chitosan.

UV-visible absorption can generally be used to analyze the content of a material. The testable material should be in liquid phase. The results can be seen in figure 6. UV-Vis characterization performed at 200-300 nm that was based on a study by Yang et al (2004) showing in the wavelength of 300-800 nm there would not be a plasmon absorbance band of metal Pt nanoparticles [13]. The curves formed from Pt/MWCNT have plasmon absorbance band at around 235 nm. The peak indicates the presence of Pt nanoparticles dispersed into 2-propanol/nafion solution. Meanwhile, the solution of PtCl$_6^{2-}$ compound has plasmon absorbance band at 265 nm indicating the presence of Pt (IV) metal content in PtCl$_6^{2-}$ compounds. This is consistent with the study of Ekrami-Kakhki et al. [7] showing that the plasmon absorbance band of Pt (IV) in PtCl$_6^{2-}$ compound is about 265 nm. When PtCl$_6^{2-}$ reacts with chitosan and NaOH, the particle of Pt (IV) will be discharged and will form colloid Pt [7].
Meanwhile, the functionalization of MWCNT (f-MWCNT) did not form a plasmon absorbance band. It could be due to quantum dot size effect as described by other [14].

![Elemental analysis of the (a) surface oxidised MWCNT and (b) Pt/CNT-chitosan.](image)

**Figure 5.** Elemental analysis of the (a) surface oxidised MWCNT and (b) Pt/CNT-chitosan.

![UV-visible absorption spectra of Pt/MWCNT, functionalized MWCNT and PtCl₂.](image)

**Figure 6.** UV-visible absorption spectra of Pt/MWCNT, functionalized MWCNT and PtCl₂²⁻.

4. Conclusion
Pt/MWCNT had been successfully synthesized in the presence of chitosan under mild condition, i.e. 80 °C. The presence of Pt nanoparticles on the surface of f-MWCNT was confirmed by XRD, EDS, and UV Vis analysis. In addition, XRD diffractogram indicated a good crystallinity of the supported nanoparticles. Calculation of average crystallite size of Pt using the Debye-Scherrer formula proved that Pt is nanoparticle. Obtained material can be employed in constructing catalyst for fuel cell.

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