

Research Article

Electrochemical Deposition of Platinum and Palladium on Gold Nanoparticles Loaded Carbon Nanotube Support for Oxidation Reactions in Fuel Cell

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Pt and Pd sequentially electrodeposited Au nanoparticles loaded carbon nanotube (Au-CNT) was prepared for the electrocatalytic study of methanol, ethanol, and formic acid oxidations. All electrochemical measurements were carried out in a three-electrode cell. A platinum wire and Ag/AgCl were used as auxiliary and reference electrodes, respectively. Suspension of the Au-CNT, phosphate buffer, isopropanol, and Nafion was mixed and dropped on glassy carbon as a working electrode. By sequential deposition method, PdPtPt/Au-CNT, PtPdPd/Au-CNT, and PtPdPt/Au-CNT catalysts were prepared. Cyclic voltammograms (CVs) of those catalysts in 1 M H₂SO₄ solution showed hydrogen adsorption and hydrogen desorption reactions. CV responses for those three catalysts in methanol, ethanol, and formic acid electrooxidations studied in 2 M CH₃OH, CH₃CH₂OH, and HCOOH in 1 M H₂SO₄ show characteristic oxidation peaks. The oxidation peaks at anodic scan contribute to those organic substance oxidations while the peaks at cathodic scan are related with the reoxidation of the adsorbed carbonaceous species. Comparing all those three catalysts, it can be found that the PdPtPt/Au-CNT catalyst is good at methanol oxidation; the PtPdPt/Au-CNT effectively enhances ethanol oxidation while the PtPdPd/Au-CNT exceptionally catalyzes formic acid oxidation. Therefore, a different stoichiometry affects the electrochemical active surface area of the catalysts to achieve the catalytic oxidation reactions.

1. Introduction

Lack of power supply with high future consuming is the problem that everyone knows that they are going to face. Fuel cells are recognized because achievement of an electric energy can directly produce from the reaction of chemical substances [1–3]. Proton exchange fuel cell (PEMFC) is a leading candidate for nowadays application but it has some problems particularly hydrogen storage. However, it can be relieved by replacing hydrogen with other liquid fuels such as methanol, ethanol, and formic acid [4, 5]. Unluckily, the slow and incomplete catalytic oxidation reactions of these organic molecules taking place at an anode are the main impediment to practical applications of the direct methanol fuel cell (DMFC), direct ethanol fuel cell (DEFC), and direct formic acid fuel cell (DFAFC) [6–8]. Pt-based materials are

currently the best electrocatalysts for these reactions. Pt alloy catalysts can enhance CO electrooxidation kinetics [4, 5, 9]. The secondary element (M) in the Pt-alloy catalysts can be attributed to the bifunctional mechanism and the electronic effect induced by the electronic interaction between Pt and M, promoting the adsorbed CO intermediate oxidation at Pt by deteriorating the metal-CO bond. The catalyst can be prepared by many preparation methods such as chemical reduction, coimpregnation, solid phase reduction, ionic liquid, vapor deposition, thermal decomposition, and electrochemical deposition methods [2, 4]. The research efforts have been dedicated to improve the Pt-based catalysts but the activity of catalysts is still insufficient. There are several serious technological challenges such as kinetic of the substances in the oxidation reactions. The oxidations have low equilibrium potentials but they need a large overpotential

to progress which depend on catalyst and operating condition [10–15]. It is well-recognized that the structure affects the activities. The different crystallographic orientations would show different activities. Therefore, the optimization of the catalyst surface can be obtained by the high performance. Alloying Pt with a second element and incorporating active cocatalysts such as adatoms are able to achieve the goal.

Moreover, Carbon support is one of the important parts to improve the fuel cell performance to achieve high power density generation and the researchers need to consider [16–18]. The high surface area of carbon with outstanding chemical and electrochemical stability, electrical conductivity, and appropriate size distribution is taken into account for metal nanoparticle catalysts to disperse on the support. With those reasons, carbon nanotube (CNT) is one of the promising that could improve a high fuel cell performance. The CNT loaded with Au nanoparticle was used as a support in this experiment as it was expected that the Au-CNT could be a good template for the coming metal atoms (Pt or Pd) to be deposited for nucleation of catalyst nanoparticle growth [19].

In this work, electrodepositions of Pt and/or Pd at Au-CNT support in metal salt aqueous solutions were performed. Differential successive electrodepositions of Pt and Pd layer at Au-CNT in electrode as a catalyst were achieved. The applications of the resulted catalysts in electrooxidations of methanol, ethanol, and formic acid are reported. Morphologies of the resulted PdPtPt/Au-CNT, PtPdPd/Au-CNT, and PtPdPt/Au-CNT catalysts were characterized by TEM. Cyclic voltammetry was used to prepare the catalysts and study their electrocatalytic properties in oxidation reactions.

2. Materials and Methods

2.1. Materials and Gold Nanoparticles Loaded CNT. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, PdCl_2 , and HAuCl_4 were obtained from Merck. Methanol, ethanol, formic acid, and sulfuric acid were received from Lab. Scan. Water was obtained from a Millipore Milli-Q water system. Gold nanoparticles were straightforwardly prepared by aqueous reduction of hydrogen tetrachloroaurate (II) with alkaline tetrakis(hydroxymethyl)phosphonium chloride [20].

2.2. Electrochemical Measurements. A glassy carbon electrode (BAS and 3.0 mm diameter) was polished with alumina slurries. The electrode was covered by ink paste which was prepared by mixing of Au-CNT, Nafion, phosphate buffer, and isopropanol and then dropped the mixture suspension onto the clean glassy carbon surface by micropipette and left the suspension to be dried for 30 min. Pt and Pd salt solutions were used as a precursor for electrodeposition on Au-CNT from the solution of 1 mM $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and PdCl_2 (dissolved in HCl solution). Voltammetric measurements were carried out with EDAQ potentiostat with a three-electrode cell system. Ag/AgCl and Pt wire were used as reference and counter electrodes, respectively. Pt and Pd metal sequential depositions were performed in the prepared precursor solutions. The catalysts were prepared on working electrode by cyclic voltammetry under potential between

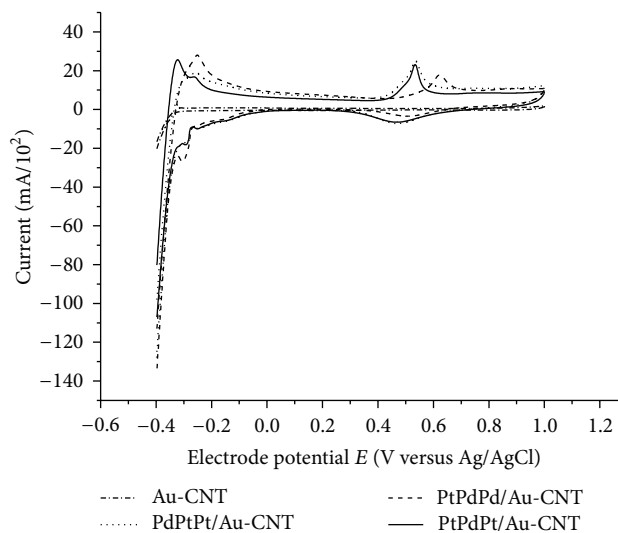


FIGURE 1: Cyclic voltammograms recorded in 1 M H_2SO_4 solution at Au-CNT, PdPtPt/Au-CNT, PtPdPd/Au-CNT, and PtPdPt/Au-CNT in the potential range -0.40 to 1.00 V at a scan rate $0.05 \text{ V} \cdot \text{s}^{-1}$.

-0.4 and 1.0 V with 3 cycles each metal solution at room temperature. The ink electrodes were used as the working electrode and the obtained catalyst electrodes were denoted as PdPtPt/Au-CNT, PtPdPd/Au-CNT, and PtPdPt/Au-CNT. The obtained catalyst electrodes were examined in 1 M H_2SO_4 solution and the solution of methanol, ethanol, and formic acid in H_2SO_4 solution (2 M CH_3OH , $\text{CH}_3\text{CH}_2\text{OH}$, and HCOOH in 1 M H_2SO_4) by CV at a scan rate of $0.05 \text{ V} \cdot \text{s}^{-1}$. Those solutions were bubbled by nitrogen gas for 20 min. and kept with N_2 atmosphere during the electrochemical experiments.

3. Results and Discussion

Three successive electrodeposited metal catalysts, PdPtPt/Au-CNT, PtPdPd/Au-CNT, and PtPdPt/Au-CNT, were prepared for electrocatalytic activity studies. CV explanations for voltammetric characterizations in H_2SO_4 and catalysis in methanol, ethanol, and formic acid oxidations are stated. Figure 1 shows general shape of CVs for Au-CNT, PdPtPt/Au-CNT, PtPdPd/Au-CNT, and PtPdPt/Au-CNT in 1 M H_2SO_4 solution at scan rate $0.05 \text{ V} \cdot \text{s}^{-1}$ in a potential window of -0.40 to 1.00 V versus Ag/AgCl. The Au-CNT electrode shows no hydrogen adsorption/desorption peak. For PdPtPt/Au-CNT, PtPdPd/Au-CNT, and PtPdPt/Au-CNT electrodes, the hydrogen adsorption/desorption peaks are defined. Hydrogen adsorption/desorption peaks for the catalysts are not totally sharp indicating that some Pt are blocked on the surface by Pd oxide. The potential region of the hydrogen adsorption/desorption (-0.10 – 0.30 V) is separated from the reversible/irreversible oxide by the double layer potential region. The double layer for those catalysts is rather similar attributed to similar metal loading amount [21, 22]. Hydrogen desorption peaks of PdPtPt/Au-CNT, PtPdPd/Au-CNT, and PtPdPt/Au-CNT are ca. -0.23 , -0.25 , and -0.35 V while

TABLE 1: Onset potentials and oxidation current intensities of PdPtPt/Au-CNT, PtPdPd/Au-CNT, and PtPdPt/Au-CNT in the potential range from 0.00 to 1.00 V at a scan rate $0.05 \text{ V}\cdot\text{s}^{-1}$.

Prepared catalyst	Methanol oxidation		Ethanol oxidation		Formic acid oxidation	
	Onset potential (V)	Anodic current intensity ($\text{mA}/10^2$)	Onset potential (V)	Anodic current intensity ($\text{mA}/10^2$)	Onset potential, x_1 (V)	Cathodic current intensity ($\text{mA}/10^2$)
PdPtPt/Au-CNT	0.30	140	0.38	245	0.10	420
PtPdPd/Au-CNT	0.38	70	0.41	235	0.01	660
PtPdPt/Au-CNT	0.30	120	0.40	265	0.10	320

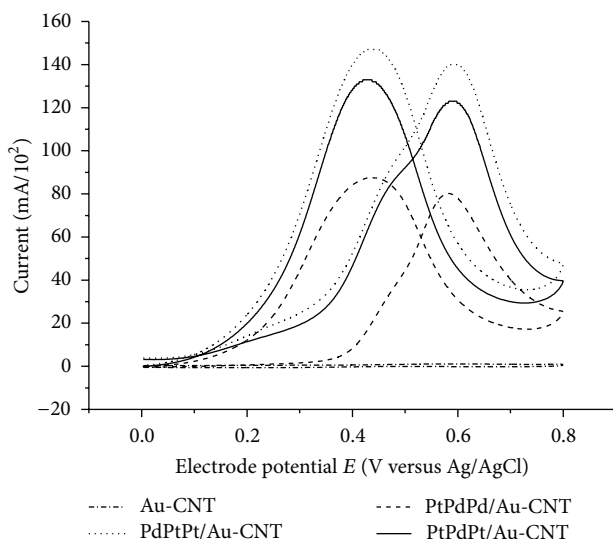


FIGURE 2: Cyclic voltammograms recorded in $2 \text{ M CH}_3\text{OH} + 1 \text{ M H}_2\text{SO}_4$ solution at Au-CNT, PdPtPt/Au-CNT, PtPdPd/Au-CNT, and PtPdPt/Au-CNT in the potential range 0.00 to 0.80 V at a scan rate $0.05 \text{ V}\cdot\text{s}^{-1}$.

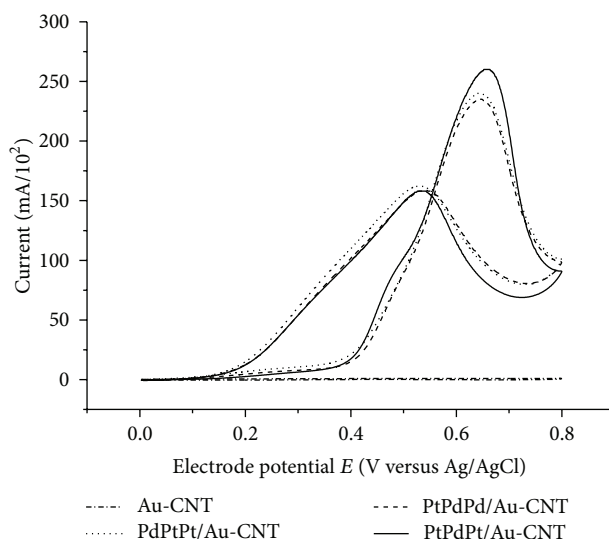


FIGURE 3: Cyclic voltammograms recorded in $2 \text{ M CH}_3\text{CH}_2\text{OH} + 1 \text{ M H}_2\text{SO}_4$ solution at Au-CNT, PdPtPt/Au-CNT, PtPdPd/Au-CNT, and PtPdPt/Au-CNT in the potential range 0.00 to 0.80 V at a scan rate $0.05 \text{ V}\cdot\text{s}^{-1}$.

the oxide potentials of those catalysts are at 0.52, 0.62, and 0.52 V, respectively. Oxide formation of PtPdPd/Au-CNT appears at higher potential as high number of Pd on the catalyst electrode. The hydrogen desorption peaks also imply electrochemically active surface area. It can be noticed that the order of deposited metal species on Au-CNT support has a different stoichiometry for hydrogen adsorption/desorption. Moreover, the current intensities associated with the reversible hydrogen adsorption/desorption region decrease to a considerable amount depending on incorporation of Pd in Pt surface matrix with lowering the charge densities in hydrogen region.

Figure 2 shows cyclic voltammograms of methanol oxidation on Au-CNT, PdPtPt/Au-CNT, PtPdPd/Au-CNT, and PtPdPt/Au-CNT in $2 \text{ M CH}_3\text{OH}$ in $1 \text{ M H}_2\text{SO}_4$ in potential range of 0.00–0.80 V versus Ag/AgCl at a scan rate of $0.05 \text{ V}\cdot\text{s}^{-1}$. The onset potential and current density of Au-CNT are hardly determined while the current intensities obtained at PdPtPt/Au-CNT, PtPdPd/Au-CNT, and PtPdPt/Au-CNT electrodes are incredibly high. Onset potentials and current intensities of the catalyst electrodes for methanol oxidation are shown in Table 1. Interestingly, the

onset potential for methanol oxidation shifts to less anodic potentials with increase in Pt depositon number. PdPtPt/Au-CNT shows highest anodic methanol oxidation with least onset potential compared with the others.

Cyclic voltammograms of ethanol electrooxidation of those catalysts were measured in $2 \text{ M CH}_3\text{CH}_2\text{OH}$ in $1 \text{ M H}_2\text{SO}_4$ solution shown in Figure 3. The voltammogram of Au-CNT shows no ethanoic oxidation peak. Voltammograms of the catalysts show a characteristic peak with oxidation peaks in the anodic scan and second oxidation peaks in the cathodic scan. The peaks of PdPtPt/Au-CNT, PtPdPd/Au-CNT, and PtPdPt/Au-CNT are ca. 0.65 V in foreword scan attributed to ethanol oxidation. The peaks at ca. 0.52 V with current intensity ca. 1.50 mA in the backward scan of those catalysts are related with the reaction of the electrode giving peak to oxidation of unreacted ethanol and absorbed intermediates. With high current density and low onset potential, PtPdPt/Au-CNT illustrates high ethanol oxidation enhancements.

Three reasons of using Pt-M alloy metal to achieve oxidations of methanol and ethanol, bifunctional oxidation mechanism, alloy electronic interaction, and leaching out

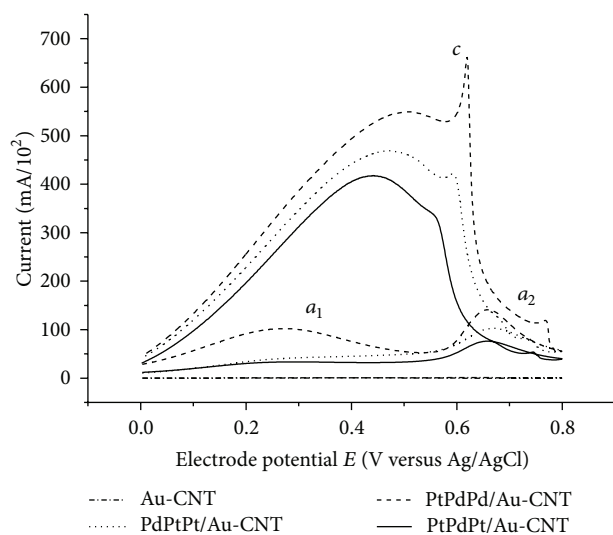
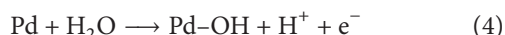
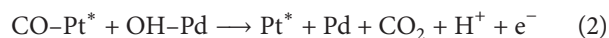


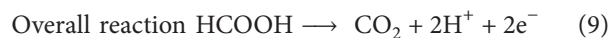
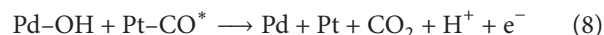
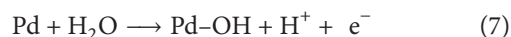
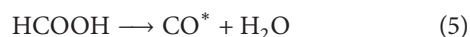
FIGURE 4: Cyclic voltammograms recorded in 2 M HCOOH + 1 M H₂SO₄ solution at Au-CNT, PdPtPt/Au-CNT, PtPdPd/Au-CNT, and PtPdPt/Au-CNT in the potential range 0.00 to 0.80 V at a scan rate 0.05 V·s⁻¹.

effect, were reported. It resulted in an increase of electrochemical active surface area [23, 24]. Electronic effect of added metal as the alloying metal modifies the electronic structure of Pt valence band and weakens CO_{ad} adsorption. This alloys CO adsorbed species is removed incredibly easily. Pt can adsorb alcohol molecules on its surface while the 2nd metal provides active surface oxides to oxidize adsorbed alcohols at low potential according to the following equations:



Please note that Pt* is active Pt on catalyst surface.

For formic acid oxidation in Figure 4, two oxidation peaks (marked as *a*₁ and *a*₂) during the forward scanning and one oxidation peak (marked as *c*) during backward scan were obtained. It shows that the electrooxidation of formic acid would follow a previous work [7, 8, 10]. This can explain that electrooxidation of HCOOH on Pt-based catalysts proceeds through a dual path mechanism which is composed of direct dehydrogenation and indirect dehydrogenation pathways. Peak *a*₁ is attributed to the oxidation of adsorbed formate in direct pathway on the catalyst active sites. Peaks *a*₂ and *c* are composed of the continuous oxidation of intermediate and adsorbed formate on CO free-Pt active sites. The anodic and cathodic current peaks and onset potentials of PdPtPt/Au-CNT, PtPdPd/Au-CNT, and PtPdPt/Au-CNT electrodes are on Table 1. The mechanism of formic acid oxidation on the catalyst electrodes is as follows:



As depicted in Figure 4, the PtPdPd/Au-CNT electrode exhibits much higher HCOOH oxidation current intensity than the others. This indicates that the incorporation of Au nanoparticles on CNT with the deposited Pt and Pd species greatly enhanced the reaction. The onset potential of the oxidation at the PtPdPd/Au-CNT electrode is rather low at ca. 0.00 V which shifts negatively compared with the others. The electrooxidation of HCOOH taking place at lower potential and onset potential shifting negatively reveals that the PtPdPd/Au-CNT electrode performed such a high catalytic activity. Pt-Pd structures are able to promote the electrochemical conversion of CO removing CO_{ads} surface poisons with increasing Pd content.

Figure 5 shows representative TEM topographic images of Au-CNT, Pt, and Pd deposited Au-CNT nanoparticle (PtPdPd/Au-CNT). The distribution of the particles is rather well dispersed with nanoparticles averaging from 5–10 nm on the CNT support. Chemical composition analysis by EDX (not shown here) indicates the presence of Pt and Pd on the Au-CNT support.

Chemical composition analysis by using EDX indicates the presence of Pt, Pd, and Au on the prepared catalysts (Figure 6). However, those 3 catalysts have different amount of Pt, Pd, and Au. An evidence of Cu content in the EDX spectra is attributed to Cu grid which is generally used for sample preparation of EDX analysis.

4. Conclusion

In this study, preparation of Pt and Pd sequentially electrodeposited Au metal nanoparticles loaded carbon nanotube (Au-CNT) was performed for the electrocatalytic study of methanol, ethanol, and formic acid oxidations. Cyclic voltammograms of catalysts, PdPtPt/Au-CNT, PtPdPd/Au-CNT, and PtPdPt/Au-CNT catalysts, showed hydrogen adsorption/desorption reactions. The hydrogen desorption peaks imply electrochemically active surface area indicating that order of metal species deposition on Au-CNT support has a different stoichiometry for the reactions. Incorporation of Pd and Pt in Au-CNT matrix would be able to alternate the current intensities for the different catalytic reactions. It can be concluded that the PtPdPt/Au-CNT catalyst is good at methanol oxidation, and the PtPdPt/Au-CNT enhances ethanol oxidation well while the PtPdPd/Au-CNT effectively catalyzes formic acid oxidation.

Conflict of Interests

The authors declare that there is no conflict of interests regarding to publication of this paper.

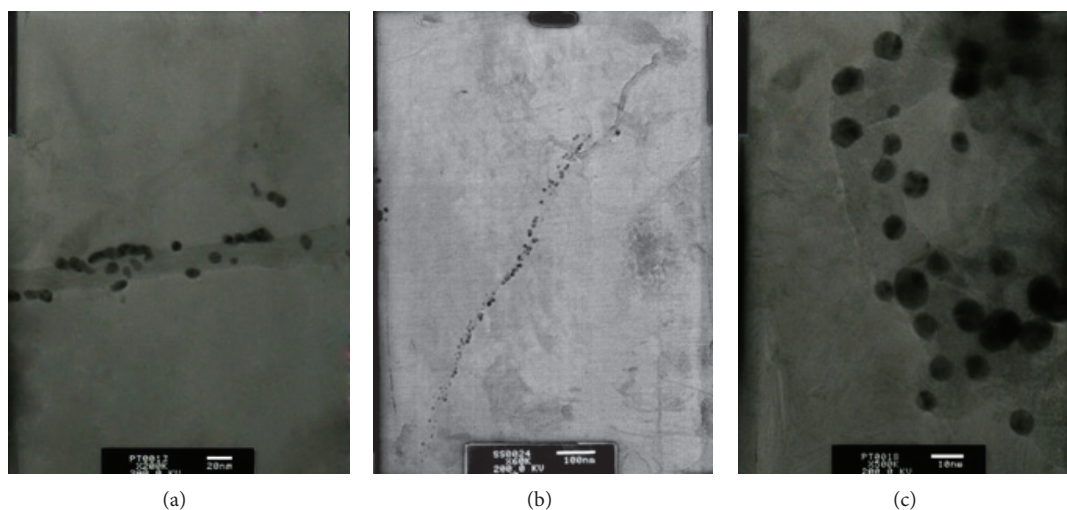


FIGURE 5: The selected TEM images of (a) Au-CNT, (b) Pt and Pd loaded Au-CNT with a closer TEM image (c).

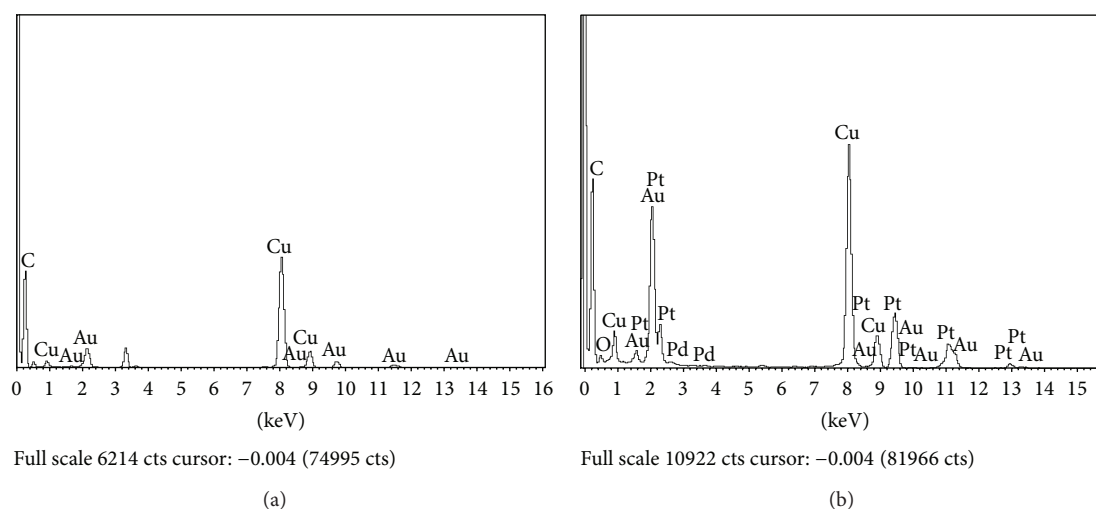


FIGURE 6: The selected EDS spectra of (a) Au-CNT and (b) Pt and Pd loaded Au-CNT.

Acknowledgments

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