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# Advantages of electrodes with dendrimer-protected platinum nanoparticles and carbon nanotubes for electrochemical methanol oxidation<sup>†</sup>

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Electrochemical sensors consisting of electrodes loaded with carbon nanotubes and Pt nanoparticles (PtNPs) protected by dendrimers have been developed using a facile method to fabricate them on two types of disposable electrochemical printed chips with a screen-printed circular gold or a screen-printed circular glassy carbon working electrode. The electrochemical performance of these sensors in the oxidation of methanol was investigated by cyclic voltammetry. It was revealed that such sensors possess stable durability and high electrocatalytic activity: the potential and the current density of an anodic peak in the oxidation of methanol increased with increasing content of PtNPs on the electrodes, indicating the promotion of electrocatalytic activity in relation to the amount of catalyst. The low anodic potential suggests the easy electrochemical reaction, and the high catalyst tolerance supports the almost complete oxidation of methanol oxidation comes from the high electrocatalytic ability of PtNPs, excellent energy transfer of carbon nanotubes and the remarkable ability of dendrimers to act as binders. Thus these systems are effective for a wide range of applications as chemical, biomedical, energy and environmental sensors and as units of direct methanol fuel cells.

## 1. Introduction

Reliable and universal analytical methods are increasingly required in a wide range of fields. Sensors are valuable detectors and have applications in medical, food, energy and environmental fields. However, in order to achieve their wide range of applications, it is necessary in some cases to develop devices with high sensitivity, rapid testing ability for a small amount of analyte and molecular recognition power. Since platinum nanoparticles (PtNPs) are known to possess unique electrocatalytic activities, they have been extensively studied with the aim of utilizing them in catalysis, chemical sensing, electrodes, and so on. PtNPs exhibit a high electrocatalytic activity in the oxidation of methanol at room temperature<sup>1–3</sup> and also show excellent electrochemical activity in the oxidation of hydrogen peroxide, which is generated from the enzymatic reaction.<sup>4,5</sup>

On the other hand, carbon nanotubes (CNTs) have been extensively used as supports for the electrocatalysts in fuel cells owing to their promising properties such as wide surface area to enlarge the electro-active surface area, excellent electrochemical durability and high electrical conductivity due to their predominant  $\pi$ -conjugated system structure.<sup>3,6–11</sup> CNT-metal nanoparticle hybrid-modified electrodes have been developed for use as fuel-cell catalysts and biosensors,6,7,12-15 and using multiwalled carbon nanotubes (MWCNTs) as catalyst supports can effectively enhance the electrocatalytic activity of PtNPs for the oxidation of methanol compared to the other carbon materials.<sup>16,17</sup> Electrocatalysts for direct methanol fuel cells (DMFCs) are prepared by electrodeposition of PtNPs on CNT electrodes using Nafion as a binder.<sup>15</sup> Although these electrocatalysts exhibit high efficiency toward the oxidation of methanol, the technique for their preparation requires costly and special equipment.

In this study, the electrochemical sensors consisting of an electrode loaded with MWCNTs and PtNPs were developed. Poly(amido amine) (PAMAM) dendrimers (DENs) have been used as protectors/stabilizers of metal/metal compound nanoparticles

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 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available: Cyclic voltammograms of CNT/DEN(PtNP)s-loaded SAM-SPCG electrodes in an aqueous 0.5 M H<sub>2</sub>SO<sub>4</sub> solution with 2 M MeOH, a plot of current density at anodic peaks against the cycle number and cyclic voltammograms of DEN(PtNP)s-loaded SPCGC electrodes in an aqueous 0.5 M H<sub>2</sub>SO<sub>4</sub> solution with 2 M MeOH. See DOI: 10.1039/c3cp43636e

#### Paper

including PtNPs and their binders on MWCNTs.<sup>18-22</sup> MWCNTs loaded with PtNPs protected by dendrimers (CNT/DENPtNPs) were loaded onto the electrodes, and the electrocatalytic activities of the sensors toward the oxidation of methanol were investigated by cyclic voltammetry (CV). This approach presents the advanced procedure for the development of electrochemical sensing systems with predominant stability and electrocatalytic activity, which are effective and versatile for a wide range of applications as sensors.

## 2. Materials and methods

#### 2.1 Reagents and materials

MWCNT and NaBH<sub>4</sub> were purchased from Wako Pure Chemical Industries Ltd. Amine-terminated fourth-generation PAMAM dendrimers (10 wt% in methanol), Na2PtCl6, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDAC) and 4-mercaptobenzoic acid (MBA) (97%) were purchased from Aldrich Chemical Co. Sulfuric acid (98%) and methyl alcohol were commercial products. All reagents were used as received. Ultra pure water was used throughout the experiments. Disposable electrochemical printed (DEP) chips (with a screen-printed circular gold (SPCG) or a screen-printed circular glassy carbon (SPCGC) working electrode) were purchased from BioDevice Technology.

#### 2.2 Fabrication of CNT/DENPtNPs on DEP chips

DENPtNPs were prepared as shown in Scheme 1(reaction a) according to the previously reported method:<sup>22</sup> an aqueous Na<sub>2</sub>PtCl<sub>6</sub> solution was mixed with a 0.2 wt% PAMAM dendrimer solution. The solution of the [PtCl<sub>6</sub>]<sup>2-</sup>-dendrimer complex was stirred for 3 days and pH was adjusted to 2. Then, an aqueous 0.3 M NaOH solution of NaBH<sub>4</sub>, which is a 10-fold mole of  $Na_2PtCl_6$ , was added to the solution of the  $[PtCl_6]^{2-}$ -dendrimer complex.

CNT/DENPtNPs were prepared by the immobilization of DENPtNPs onto acid-treated MWCNTs through the amidation process as shown in Scheme 1(reaction b):<sup>22</sup> the acid-treated MWCNTs (20 mg), which were prepared using the method previously reported,<sup>18</sup> were dispersed in the DENPtNPs solution (5 cm<sup>3</sup>) and the mixtures were stirred for 1 h at room temperature. Then, EDAC was added to the mixtures and the mixtures were vigorously stirred at room temperature for 2 days to allow the amide formation. The dispersion was then filtered using a Millipore filter membrane (PTFE, pore size =  $0.2 \mu m$ ). The filtered residue was washed with water several times and dried overnight at 110 °C.

A self-assembled monolayer (SAM) of carboxyl-terminated thiol on an Au electrode was fabricated as follows:<sup>22-24</sup> a SPCG DEP chip was immersed horizontally into a 20 mM ethanol solution of MBA for 24 h at room temperature. After that, excess of MBA on the SPCG electrode was removed by rinsing with ethanol followed by water, and then the SAM-SPCG DEP chip was dried overnight in a vacuum oven. For the chemical immobilization of CNT/DENPtNPs onto the SAM-modified electrode, an aqueous 10 mg cm<sup>-3</sup> dispersion (10 mm<sup>3</sup>) of CNT/DENPtNPs was added to EDAC and retained overnight on the SAM-SPCG electrode as shown in Scheme 1 (reaction c). The adsorption of CNT/DENPtNPs onto the SPCGC electrode was carried out by retaining an aqueous dispersion of CNT/DENPtNPs on the SPCGC electrode overnight. The microscopic observation of CNT/DENPtNPs was performed using a transmission electron microscope (TEM), Hitachi H-7000, equipped with a CCD camera, operating at a voltage of 100 kV. The surface morphologies of CNT/DENPtNPs on the SAM-SPCG and SPCGC electrodes were characterized using a field emission-scanning electron microscope (FE-SEM), JEOL JSM-6500F, operating at a voltage of 20 kV.

#### 2.3 Measurements of electrocatalytic activity

Electrocatalytic activities of CNT/DENPtNPs on the DEP chips were examined using a Hokuto-Denko HZ-3000. The DEP chips



Scheme 1 Schematic illustration of fabrication of CNT/DENPtNPs on SAM-SPCG electrodes.

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equipped carbon as a counter electrode, Ag/AgCl as a reference electrode and gold or glassy carbon as a working electrode (SPCG or SPCGC electrode, respectively). The working areas of the SPCG and SPCGC electrodes were 3.67 and 2.64 mm<sup>2</sup>, respectively. The DEP chips were supported vertically during the CV measurement. Electrochemical measurement was carried out in 2 cm<sup>3</sup> of an aqueous 0.5 M H<sub>2</sub>SO<sub>4</sub> solution including 2.0 M CH<sub>3</sub>OH, where the circular area of the working electrode was immersed. The potential of CV was scanned between -0.2and 1.2 V at a scan rate of 20 mV  $s^{-1}$  at room temperature. All measurements were carried out for 20 cycles and the data at the 20th cycle were collected except for the analysis of the number of cycles. Electrical current density  $(mA cm^{-2})$  was calculated by normalizing electrical current (mA) on the working area of the SPCG and SPCGC electrodes. In the plot of current density against the cycle number or in the calculation of catalyst tolerance (the ratio of the current density of the forward anodic peak to the current density of the reverse anodic peak), the observed current densities at redox peaks were subtracted from the corresponding current densities on bare electrodes without CNT/DENPtNPs or DENPtNPs in an aqueous 0.5 M H<sub>2</sub>SO<sub>4</sub> solution with 2.0 M CH<sub>3</sub>OH in order to delete the contribution of the non-Faraday current.

## 3. Results and discussion

# 3.1 Structure of PtNPs and durability and reactivity of CNT/DENPtNPs-loaded electrodes

Platinum nanoparticles, PtNPs, were synthesized by reducing the platinum precursor in the presence of PAMAM dendrimers at five different molar ratios of  $Na_2PtCl_6$  to amine terminal groups of PAMAM dendrimers (M:D = 0.1:1, 0.2:1, 0.3:1, 0.4:1 and 0.5:1) at the constant dendrimer concentration (0.2 wt%). Pt nanoparticles protected by dendrimers, DENPtNPs, were only 2–3 nm in diameter at 0.1:1 and 0.2:1, as seen in Fig. 1(a), but aggregated or precipitated at higher M:D ratios because of the less concentration of dendrimers to protect nanoparticles. Successively DENPtNPs were loaded on CNT/ DENPtNPs but the distribution of PtNPs on CNTs reflected their distribution state in water as exemplified in Fig. 1(b).

The surface morphologies of the SAM-SPCG and SPCGC electrodes before and after the fabrication of CNT/DENPtNPs at M: D = 0.2: 1 were observed by FE-SEM. Fig. 2(a) indicates the deposition of spherical gold particles on the SPCG working electrode, while glassy carbon nanosheets with nanosized voids were observed on the SPCGC working electrode (Fig. 2(b)). It is clearly seen in Fig. 2(c) and (d), respectively, that fiber-like structures of CNT/DENPtNPs were successfully fabricated on the surfaces of SAM-SPCG and SPCGC working electrodes.

# 3.2 Electrocatalytic activity of SAM-SPCG electrodes toward methanol oxidation

The electrocatalytic activity of DENPtNPs-loaded SAM-SPCG electrodes toward methanol oxidation in an aqueous solution including 0.5 M  $H_2SO_4$  and 2 M  $CH_3OH$  was investigated by CV. Fig. 3(a) shows the CV results for 20 cycles with



**Fig. 1** TEM images of (a) DENPtNPs and CNT/DENPtNPs at M:D = 0.2:1 (b) before and (c) after the oxidation reaction of methanol for 20 cycles on a SPCG electrode. CNT/DENPtNPs after the reaction were scratched from the SPCG electrode and utilized for TEM observation.



Fig. 2 Surface morphologies of working electrodes. (a) Bare SPCG, (b) bare SPCGC, (c) CNT/DENPtNPs-loaded SAM-SPCG, (d) CNT/DENPtNPs-loaded SPCGC. DENPtNPs were prepared at M: D = 0.2: 1.

DENPtNPs-loaded SAM-SPCG electrodes. The CV at each M:D ratio shows an anodic peak at 0.38 to 0.58 V in the forward scan.



Fig. 3 (a) Cyclic voltammograms of DENPtNPs-loaded SAM-SPCG electrodes in an aqueous  $0.5 \text{ M H}_2\text{SO}_4$  solution with 2 M MeOH and (b) a plot of current density (compensated for non-Faraday current) at an anodic peak against the cycle number. M: D:  $\bullet$  0.1: 1,  $\bigcirc$  0.2: 1,  $\bigvee$  0.3: 1,  $\triangle$  0.4: 1,  $\blacksquare$  0.5: 1.

Stability of DENPtNPs-loaded electrodes during electrochemical reaction was evaluated by repeating up to 20 CV scans over the total scanning time of 90 min. No abnormality was observed in the CV profiles, and the current density of the anodic peak in the forward scan increased with the increasing number of CV scans as seen in Fig. 3(b). It was also confirmed from TEM observation (Fig. 1(c)) that DENPtNPs stably bound on MWCNTs even after the methanol oxidation reaction for 20 cycles. These observations suggest that DENPtNPs-loaded electrodes possess the high and long-term stability during the electrochemical methanol oxidation. It can be noted that the current density of the anodic peak still increases over 20 cycles, especially, at high M:D ratios, as seen in Fig. 3(b). This indicates that the activity of the oxidation of methanol increases over multiple cycles or time periods. The dendrimer-poisoning of the Pt nanoparticles is one of the possibilities<sup>25,26</sup> but the DENPtNPs may not be poisoned by the dendrimers. Since the present reaction is carried out in water, that is, in "a good solvent",

it can be assumed that the electrocatalytic activity of DENPtNPs increases with multiple cycles due to the slow diffusion of methanol into dendrimers<sup>27</sup> to attain the active sites of Pt nanoparticles.

In the methanol oxidation reaction, methanol is oxidized to carbon dioxide according to the following reaction by means of a catalyst (in the present case, PtNPs):  $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ . Then the current density of an anodic peak is directly proportional to the amount of methanol oxidized at the electrode.<sup>17</sup> However, by-products such as formaldehyde, formic acid, carbon monoxide and other intermediate carbonaceous species are formed and adsorbed on the surface of the electrode, leading to a decrease in the methanol oxidation reaction and hence the reduction of the current density.<sup>28,29</sup> Therefore, the efficient electrocatalyst must allow complete oxidation of methanol and/or intermediate carbonaceous species to carbon dioxide so as to produce higher current density at low potential. The oxidation potential and current density of an anodic peak

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**Fig. 4** (a) Potential and (b) current density of anodic peaks against M:D. Electrodes: ● DENPtNPs-loaded SAM-SPCG, ▲ CNT/DENPtNPs-loaded SAM-SPCG, □ DENPtNPs-loaded SPCGC, ▽ CNT/DENPtNPs-loaded SPCGC. The peak current density is compensated for non-Faraday current.

in a CV curve are often used to determine the activity of the electrocatalyst toward methanol oxidation.<sup>30,31</sup> The potential and current density of an anodic peak after 20 CV scans of methanol oxidation are plotted as a function of the M:D ratio as shown in Fig. 4 and listed in Table S1 (ESI<sup>†</sup>). It was found that the peak shifted to the higher potential from 0.38 to 0.58 V, and its current density also significantly increased from 0.41 to 2.57 mA cm<sup>-2</sup> with the M:D ratio. A lower potential of the anodic peak indicates that the methanol oxidation occurs more easily on the electrode, and the increase in the current density of the anodic peak is directly attributed to the electrocatalytic activity of the PtNPs toward methanol oxidation.

Meanwhile, a small anodic peak attributed to the removal of the incompletely oxidized carbonaceous species formed during the forward scan<sup>1,11,32</sup> was observed at around 0.08 and 0.24 V for the DENPtNPs-loaded electrodes at M: D = 0.4: 1 and 0.5: 1, respectively, in the reverse scan. The appearance of this anodic peak in the reverse scan indicates that the catalyst surface becomes poisoned by the deposition of carbonaceous species. The ratio of the current density  $(I_{\rm F})$  of a forward anodic peak to the current density  $(I_R)$  of the reverse anodic peak,  $I_F/I_R$ , can be used to denote the catalyst tolerance to the deposition of carbonaceous species.<sup>11,29</sup> All the relevant data are listed in Table S1 (ESI<sup>+</sup>). The  $I_{\rm F}/I_{\rm R}$  value of DENPtNPs-loaded electrodes slightly decreased (from 6.33 to 4.94) with the M:D ratio (from 0.4:1 to 0.5:1); however, these  $I_F/I_R$  values are still higher than that of the commercial Johnson Matthey PtRu/C (JM-PtRu/C) catalyst  $(I_F/I_R = 2.8)$ .<sup>33</sup> The high  $I_F/I_R$  ratio indicates that DENPtNPs-loaded electrodes have a high catalyst tolerance to the deposition of carbonaceous species on the catalyst surface during the methanol oxidation as compared to the commercial catalyst.

When CNT/DENPtNPs were loaded on SAM-SPCG electrodes instead of DENPtNPs, the CVs for methanol oxidation revealed only a very small anodic peak at around 0.39-0.52 V in the forward scan, as shown in Fig. S1(a) (ESI<sup>+</sup>), while the anodic peak in the reverse scan was hardly observed. However, the durability of these electrodes was still adequate, as the current in the forward scan gradually increased with the CV scan, as seen in Fig. S1(b) (ESI<sup>+</sup>). Moreover, the current slightly increased (from 0.14 to 0.32 mA  $\text{cm}^{-2}$  at 20 scans) with the M:D ratio. Meanwhile, an anodic peak at around 0.95 V and a cathodic peak at around 0.72 V were always detected with similar current at every M: D ratio. Similar peaks were observed even on CNT-loaded SAM-SPCG electrodes without Pt catalysts (see Fig. S1(a), ESI<sup>†</sup>). These redox peaks can be attributed to the formation of gold oxide and its subsequent removal by reduction, respectively.34 This observation indicates that the electrochemistry of the gold electrode and the oxidation of methanol occur at the same time and the redox of the gold electrode is dominant over the methanol oxidation. Compared to CNT/DENPtNPs-loaded SAM-SPCG electrodes, in the case of DENPtNPs-loaded SAM-SPCG electrodes, redox peaks of gold were observed at low M: D values but superposed by intensified peaks of methanol oxidation at high M:D values (see Fig. 3(a)).

The disappearance of the gold redox peaks during the oxidation of methanol in the case of DENPtNPs-loaded SAM-SPCG electrodes is similar to the electrochemical characteristics of Pt-decorated nanoporous gold (NPG) leaf electrodes in an acid solution.<sup>35</sup> It has been reported that the nearly complete coverage of Pt on the surface of NPG electrodes almost suppresses the gold redox peaks due to the strong interaction between Au substrates and Pt thin layers and can strengthen the bonding between Pt and oxygen-containing species  $(SO_4^{-})$ . Hence, Pt becomes more active in the electrochemical reaction than the Au electrode. Correspondingly, in the case of DENPtNPs-loaded SAM-SPCG electrodes, the interaction between PtNPs and Au electrodes is strong enough, since PtNPs and Au electrodes are distanced as short as only the intervened thickness of binders (dendrimers). Thus Pt actively reacts in methanol oxidation with the suppression of gold redox peaks. On the other hand, in the case of CNT/DENPtNPs-loaded SAM-SPCG electrodes, the interaction between PtNPs on CNTs and SPCG electrodes might not be strong enough, since many PtNPs are located on CNTs loaded on electrodes. Hence the suppression effect of PtNPs on gold redox signals is very low and the gold redox signals dominantly arise in electrochemical reaction on CNT/DENPtNPs-loaded SPCG electrodes.

# 3.3 Electrocatalytic activity of SPCGC electrodes toward methanol oxidation

The evaluation of electrocatalytic activity toward methanol oxidation was also carried out using SPCGC electrodes in place

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Fig. 5 (a) Cyclic voltammograms of CNT/DENPtNPs-loaded SPCGC electrodes in an aqueous 0.5 M  $H_2SO_4$  solution with 2 M MeOH and (b) a plot of current density (compensated for non-Faraday current) at an anodic peak against the cycle number. CNT-loaded: •. CNT/DENPtNPs-loaded (M:D): • 0.1:1,  $\forall$  0.2:1,  $\triangle$  0.3:1,  $\blacksquare$  0.4:1,  $\Box$  0.5:1.

of SAM-SPCG electrodes. The resultant CVs for 20 cycles on CNT/DENPtNPs-loaded SPCGC electrodes are shown in Fig. 5(a). The anodic peak occurred at around 0.39–0.53 V in the forward scan, and the electrode at each M:D ratio also possessed a high stability toward the electrochemical reaction, as observed from the results that the current in the forward scan was nearly constant (M:D = 0.1:1 and 0.2:1) or gradually increased (M:D = 0.3:1–0.5:1) with the cycle number of the CV scan as seen in Fig. 5(b).

It has been reported that the electrocatalytic activity of the catalyst is influenced by the composition, the content and the activity efficiency of the electrocatalyst, leading to the required current.<sup>2</sup> Although the potential of the anodic peak after 20 CV scans slightly increased with the M : D ratio, as seen

in Fig. 4(a) and Table S1 (ESI<sup>†</sup>), the oxidation of methanol on the CNT/DENPtNPs-loaded SPCGC electrodes still occurred at lower potential than the previous reports,<sup>2,30</sup> indicating the easy methanol oxidation: Pt-MWCNT and Pt–Si-MWCNT electrodes, which were prepared by vacuum pyrolysis of a Pt precursor on MWCNT and deposition of PtNPs on silanemodified MWCNTs, respectively, oxidized methanol at the potentials of 0.74 (ref. 2) and 0.76 (ref. 30) V, respectively. In addition, the current density of the anodic peak from this electrode significantly increased (from 0.25 to 2.19 mA cm<sup>-2</sup>) with the M:D ratio (see Fig. 4(b) and Table S1, ESI<sup>†</sup>). These results suggest that the CNT/DENPtNPs play an important role in the promotion of the oxidation of methanol on the SPCGC electrode. The anodic peak in the reverse scan of CNT/DENPtNPsloaded SPCGC electrodes was observed at around 0.05–0.11 V after 20 CV scans for CNT/DENPtNPs of M:D = 0.3:1–0.5:1. The calculated  $I_F/I_R$  value increased (from 4.24 to 8.11) as the M:D ratio increased (from 0.3:1–0.5:1) (see Table S1, ESI†). These results indicate that the CNT/DENPtNPs have high catalyst tolerance to the deposition of carbonaceous species in comparison with the previous reports,<sup>2,30</sup> where the  $I_F/I_R$ values of Pt-MWCNT and Pt-Si-MWCNT catalysts were 0.75 (ref. 2) and 1.8 (ref. 30).

The high current density of the anodic peak in the forward scan and the high  $I_{\rm F}/I_{\rm R}$  value observed on CNT/DENPtNPs-loaded SPCGC electrodes indicate that methanol is almost completely oxidized to carbon dioxide but a few carbonaceous species are adsorbed after the forward scan. These observations suggest that the electrodes possess high stability and electrocatalytic activity toward the oxidation of methanol.

The CVs of DENPtNPs-loaded SPCGC electrodes at M:D = 0.1:1-0.3:1 for the oxidation of methanol revealed anodic peaks at around 0.30–0.54 V in the forward scan and at around 0.16–0.23 V in the reverse scan, as seen in Fig. S2 (ESI†). The current slightly increased (from 0.02 to 0.68 mA cm<sup>-2</sup> at 20 scans) with the M:D ratio. The calculated  $I_F/I_R$  value increased from 2.28 to 3.10 at M:D = 0.2:1 to 0.3:1 (see Table S1, ESI†). It was observed that the current density obtained from DENPtNPs-loaded SPCGC electrodes was lower than CNT/DENPtNPs-loaded SPCGC electrodes at the same M:D. Thus, it can be inferred that CNTs effectively enhance the catalytic activity of PtNPs for the oxidation of methanol.

The evaluation of electrocatalytic activity on CNT/ DENPtNPs-loaded SPCGC electrodes was also performed in an aqueous  $0.5 \text{ M H}_2\text{SO}_4$  solution with 0.1 M MeOH and compared with 2 M MeOH. As seen in Fig. S3 (ESI<sup>†</sup>), while the oxidation of methanol was hardly observed in the CV of the M : D ratio at 0.1:1, the CV of the M : D ratio at 0.3:1 and 0.5:1 showed an anodic peak at 0.38 to 0.58 V in the forward scan. In addition, it was observed that the activity of the CNT/DENPtNPs on SPCGC in the oxidation of methanol also increased over multiple cycles or time periods even though the concentration of the methanol is lesser (0.1 M), although the current density was lower for 0.1 M MEOH than for 2 M MEOH. Thus, these results reveal that the difference in the detection of methanol oxidation between 0.1 and 2 M MEOH comes from the difference in the concentration of methanol composition. However, if the content of the catalyst (Pt) is elevated, the high sensitivity for the detection of methanol oxidation is affected even for dilute methanol content (0.1 M MEOH).

Table 1 summarizes the electrocatalytic activity of PtNPs in the oxidation of methanol on the catalyst support using electrodes prepared by different methods.<sup>3,9,16,36,37</sup> It can be noted that CNT/DENPtNPs-loaded electrodes revealed lower potentials of an anodic oxidation peak and the higher catalyst tolerance to the deposition of carbonaceous species on the catalyst surface than the other PtNP systems on carbon supports. It is suggested from this comparison that the present electrodes are good candidates as electrocatalysts for DMFCs.

### 4. Conclusions

Hybrids of DENPtNPs and CNT/DENPtNPs with different M:D values, namely, different PtNP contents were successfully loaded on SPCGC and SAM-SPCG electrodes through adhesion and chemical binding, respectively. The electrodes possessed high stability (durability), since DENPtNPs and CNT/DENPtNPs still retained their physical and chemical immobilization on the DEP chips through binders/stabilizers even after 20 cycles of the CV scan. Therefore G4 PAMAM dendrimers play an important role as stabilizers and binders in electrodes. Meanwhile, these electrodes revealed high electrochemical activity, since PtNPs and CNTs in the hybrids promoted the electrocatalytic reaction and the electron transfer between the electrodes and the redox species in the solution phase. The molecular length of SAM on SPCG also affects the electrocatalytic activity: 4-mercaptobenzoic acid SAM-modified electrodes displayed the electrocatalytic activity<sup>22</sup> but mercaptoundecanoic acid SAMmodified electrodes did not.38

The electrocatalytic activities toward the oxidation of methanol were compared among four types of electrodes. The electrodes revealed, in common, lower potential of anodic peaks at around 0.38-0.58 V in the forward scan than that reported in the literature (0.66-0.85 V),<sup>3,9,16,36,37</sup> where PtNPs were commonly loaded on the catalyst supports, as seen in Table 1. This means that the oxidation reaction of methanol occurs easily on the

Anodic peaks at forward and reverse scans of PTNPs on the catalyst support prepared by different methods and electrodes toward the oxidation of methanol				
Electrodes	Preparation	Oxidation peak (V)		
		Forward	Reverse	Ref.
Optically transparent electrodes (OTEs) coated by SWCNT film	Electrodeposition of Pt NPs	0.80	0.65	16
Glassy carbon disk	Drop-casting of carbon-supported Pt and Pt–Au NPs in Nafion <sup>®</sup>	0.67-0.72	0.50-0.58	36
Glassy carbon rotating disk	Deposition of DEN(Pt)s in Nafion	0.85	0.65	9
Glassy carbon disk	Drop-casting of Pt/MWCNT	0.70	0.50	37
MWCNT-modified glassy carbon	Electrodeposition and dip-coating of Pt NPs	0.66	0.47	3
SPCGC in DEP chips	Physical immobilization of CNT/DENPtNPs or DENPtNPs through dendrimer binders	0.30-0.54	0.16-0.23	Present study
SPCG in DEP chips	Chemical immobilization of CNT/DENPtNPs or DENPtNPs through dendrimer binders	0.38-0.58	0.08-0.24	Present study

Table 1 Anodic peaks at forward and reverse scans of PtNPs on the catalyst support prepared by different methods and electrodes toward the oxidation of methanol

present electrodes. It should also be noted that the potential of an anodic peak in the forward scan increased with increasing content of PtNPs without a significant difference among four electrodes, indicating the promotion of electrocatalytic activity in relation to the amount of catalyst.

The current density of the anodic peak in the forward scan increased with increasing content of PtNPs for three electrodes except for CNT/DENPtNPs-loaded SAM-SPCG electrodes. This result suggests that PtNPs play an important role as a catalyst in the promotion of the oxidation of methanol, since the current density at an anodic peak is directly proportional to the amount of methanol oxidized at the electrode. A weak anodic peak in the reverse scan appeared at around 0.08-0.24 V against 0.47-0.65 V from the literature (Table 1).<sup>3,9,16,36,37</sup> The ratio of current densities of anodic peaks in forward and reverse scans,  $I_{\rm F}/I_{\rm R}$ , is the barometer of catalyst tolerance to the deposition of carbonaceous species on the catalyst surface during the oxidation of methanol. The calculated values (2.3-8.1) for three electrodes except for CNT/DENPtNPs-loaded SAM-SPCG electrodes, as seen in Table S1 (ESI<sup>†</sup>), are higher than the values calculated from the literature (0.7–3.0),<sup>3,9,16,36,37</sup> suggesting that methanol is almost completely oxidized to carbon dioxide and some carbonaceous species are adsorbed after the forward scan on these three electrodes.

In the case of the electrocatalytic activity of CNT/DENPtNPsloaded SAM-SPCG electrodes toward the oxidation of methanol, although the electrochemistry of the gold electrode and the oxidation of methanol occur at the same time, the redox reaction of gold electrodes is dominant over the oxidation of methanol at the electrode. This result suggests that the type of electrode used in the electrochemical reaction influences the electrocatalytic activity.

The present investigation indicates the remarkable stability and electrocatalytic activity of the present electrodes for target molecules, if the adequate reaction system is loaded on the electrodes. Moreover, the DEP chips are adequate for a small amount of analytes and rapid testing. Therefore, the present approach provides the advanced development of effective and versatile electrochemical systems for a wide range of applications as chemical, energy, biomedical and environmental sensors and moreover as units of DMFC systems.

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# References

1 J. Huang, Z. Liu, C. He and L. M. Gan, *J. Phys. Chem. B*, 2005, **109**, 16644–16649.

- 2 Y. J. Gu and W. T. Wong, Langmuir, 2006, 22, 11447-11452.
- 3 P. Yu, Q. Qian, Y. Lin and L. Mao, *J. Phys. Chem. C*, 2010, **114**, 3575–3579.
- 4 A. Guerrieri and F. Palmisano, Anal. Chem., 2001, 73, 2875–2882.
- 5 R. S. Dey and C. R. Raj, J. Phys. Chem. C, 2010, 114, 21427-21433.
- 6 L. Su, F. Gao and L. Mao, Anal. Chem., 2006, 78, 2651-2657.
- 7 A. L. M. Reddy and S. Ramaprabhu, *J. Phys. Chem. C*, 2007, 111, 16138–16146.
- 8 J. Okuno, K. Maehashi, K. Matsumoto, K. Kerman,
  Y. Takamura and E. Tamiya, *Electrochem. Commun.*, 2007,
  9, 13–18.
- 9 J. Ledesma-Garcia, I. L. Escalante Garcia, F. J. Rodriguez, T. W. Chapman and L. A. Godinez, *J. Appl. Electrochem.*, 2008, 38, 515–522.
- M. U. Ahmed, M. M. Hossain and E. Tamiya, *Electroanalysis*, 2008, 20, 616–626.
- 11 M. Okamoto, T. Fujigaya and N. Nakashima, *Fuel Cells*, 2009, 5, 735–740.
- 12 W. Lin, F. Lu and J. Wang, *Electroanalysis*, 2004, 16, 145–149.
- 13 G. Liu, S. L. Riechers, M. C. Mellen and Y. Lin, *Electrochem. Commun.*, 2005, 7, 1163–1169.
- 14 M. Yang, Y. Yang, Y. Liu, G. Shen and R. Yu, Biosens. Bioelectron., 2006, 21, 1125–1131.
- 15 G. Wu and B. Xu, J. Power Sources, 2007, 174, 148-158.
- 16 G. Girishkumar, K. Vinodgopal and P. V. Kamat, J. Phys. Chem. B, 2004, 108, 19960–19966.
- 17 L. Dong, R. R. S. Gari, Z. Li, M. M. Craig and S. Hou, *Carbon*, 2010, 48, 781–787.
- 18 X. Lu and T. Imae, J. Phys. Chem. C, 2007, 111, 2416-2420.
- 19 X. Lu and T. Imae, J. Phys. Chem. C, 2007, 111, 8459-8462.
- 20 G. Vijayaraghavan and K. J. Stevenson, *Langmuir*, 2007, 23, 5279–5282.
- 21 M. A. Herrero, J. Guerra, V. S. Myers, M. V. Gómez, R. M. Crooks and M. Prato, ACS Nano, 2010, 4, 905.
- A. Siriviriyanun and T. Imae, *Phys. Chem. Chem. Phys.*, 2012, 14, 10622–10630.
- 23 T. Yamazaki and T. Imae, J. Nanosci. Nanotechnol., 2005, 5, 1066–1071.
- 24 T. Yamazaki, T. Imae, H. Sugimura, N. Saito, K. Hayashi and O. Takai, *J. Nanosci. Nanotechnol.*, 2005, 5, 1792–1800.
- 25 L. Sun and R. M. Crooks, Langmuir, 2002, 18, 8231-8236.
- 26 R. W. J. Scott, O. M. Wilson and R. M. Crooks, *J. Phys. Chem. B*, 2005, **109**, 692–704.
- 27 H. Ye and R. M. Crooks, J. Am. Chem. Soc., 2005, 127, 4930-4934.
- 28 A. S. Arico, S. Srinivasan and V. Antonucci, *Fuel Cells*, 2001, 1, 133–159.
- 29 Y. Lu and R. G. Reddy, Int. J. Hydrogen Energy, 2008, 33, 3930-3937.
- 30 D. J. Guo and S. K. Cui, J. Solid State Electrochem., 2008, 12, 1393–1397.

- 31 P. Qian, S. Ai, H. Yin and J. Li, *Microchim. Acta*, 2010, **168**, 347–354.
- 32 S. W. Lee, S. Chen, W. Sheng, N. Yabuuchi, Y. Kim, T. Mitani, E. Vescovo and Y. Shao-Horn, *J. Am. Chem. Soc.*, 2009, **131**, 15669–15677.
- 33 S. H. Liu, W. Y. Yu, C. H. Chen, A. Y. Lo, B. J. Hwang,
  S. H. Chien and S. B. Liu, *Chem. Mater.*, 2008, 20, 1622–1628.
- 34 G. Liu, T. Bocking and J. J. Gooding, *J. Electroanal. Chem.*, 2007, **600**, 335–344.
- 35 X. Ge, R. Wang, P. Liu and Y. Ding, *Chem. Mater.*, 2007, **19**, 5827–5829.
- 36 G. Selvarani, S. V. Selvaganesh, S. Krishnamurthy, G. V. M. Kiruthika, P. Sridhar, S. Pitchumani and A. K. Shukla, *J. Phys. Chem. C*, 2009, **113**, 7461–7468.
- 37 S. H. Lee, K. Teshima, I. Y. Jang, Y. Sonobayashi, H. Sugimura, M. Endo and S. Oishi, *Fuel Cells*, 2010, **10**, 221–226.
- 38 S.-K. Oh, Y.-G. Kim, H. Ye and R. M. Crooks, *Langmuir*, 2003, 19, 10420–10425.