



# Hydrogen evolution reaction efficiency by low loading of platinum nanoparticles protected by dendrimers on carbon materials



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## ABSTRACT

Efficiency of hydrogen evolution reaction (HER) was evaluated with a small amount of platinum nanoparticles (PtNPs) immobilized on graphene oxides, carbon nanohorns (CNHs) and carbon nanotubes (CNTs) through dendrimer (Den)-mediated chemical reaction. The excellent HER, durability and stability of composite electrodes are due to chemical bonding immobilization of PtNPs on carbon materials and its substantial graphitized structure. Thus, CNH/DenPtNPs and CNT/DenPtNPs are the promising nano-electrocatalysts with low onset potential and high cathodic current density for HER and their high activities are achieved at only ~1 wt% of PtNPs.

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## 1. Introduction

Focusing on global activities, consumption of fossil fuels has led to diverse environmental issues. In this view, there have been challenges to discovering sustainable, clean and environmentally-friendly fuels. Hereupon, hydrogen is an inspiring alternative fuel and energy carrier, being free from CO<sub>2</sub> emission [1]. The successful attaining of hydrogen production from the electrocatalytic hydrogen evolution reaction (HER) method must be keeping the clean environment rather than the steam-methane reforming process [2]. In this respect, the modern research involves the development of nano-electrocatalysts towards superior HER [3].

Even though platinum is an electrocatalyst of prime quality in HER, its high cost and low abundance have stimulated the development of alternative electrocatalysts [4]: Over the past decades, nickel-based electrocatalysts such as Ni<sub>2</sub>P [5], NiS [6] and molybdenum materials including MoP [7], MoS<sub>2</sub> [8] and Mo<sub>2</sub>C [9] have been engaged in HER. However, none of these attempts has achieved a HER efficiency obtained from a 40 wt% Pt-on-charcoal (Pt/C)-modified electrode. Therefore, the major conclusion is to reduce the content of Pt and make composites with highly active materials for HER electrocatalysis.

Carbon-based electrocatalysts have been exploited in energy systems due to their unique electronic, mechanical and optical properties [10–12]. However, metallic nanoparticle-modified carbon materials readily act as conductive scaffolds as well as intensifiers on the electrocatalysis of metallic nanoparticles [13,14]. Meanwhile, poly(amido amine) (PAMAM) dendrimers have enough void volume

in their spherical shape to encapsulate solvents, small molecules, etc. unlike conventional linear polymers [15] and shown potential in synthesizing size-controlled metal nanoparticles through complexation of metal precursors with their amine groups [16]. Thus, PAMAM dendrimers encapsulated metal nanoparticles have been emerged in electrocatalysis due to their intriguing properties [17–19]. However, to the best of our knowledge, there is no report for using dendrimers encapsulated Pt nanoparticles (PtNPs) on carbon materials towards HER.

In this report, HER was efficiently examined using electrocatalyst systems containing ~1 wt% of PtNPs protected by PAMAM dendrimers, which were loaded on graphene oxides (GOs), carbon nanohorns (CNHs) and carbon nanotubes (CNTs) through chemical linkage. The HER parameters from Tafel analysis were discussed in comparison with loading amount of PtNPs. This study will demonstrate the high HER efficiency from low amount of Pt and contribute to the development of low cost hydrogen energy/battery systems. Moreover, it should be noticed that the strategy of this investigation is based on the concept of nanoarchitectonics for energy generation [20,21].

## 2. Experimental

Synthesis of DenPtNPs was followed the procedure previously reported [22]. Briefly, Pt precursor (Na<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, 1 mM) was added to an aqueous solution (0.2 wt%, 10 ml) of PAMAM dendrimer (amine-terminated fourth-generation). During constant stirring at pH 4, the mixture was added dropwise a 0.3 M sodium hydroxide solution (1 ml) of sodium borohydride (10 mM) and the stirring was continued for overnight. The formation of DenPtNPs was confirmed from the appeared black color of the solution.

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Commercial multi-walled CNT and single-walled CNH were functionalized by acid treatment as per previous report [16]. The aqueous dispersion (1 mg/ml) of acid-functionalized CNT and CNH and commercial GO were sonicated 1 h and stirred with 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (3.45 mg/ml) and N-hydroxysuccinimide (5.2 mg/ml) for 2 h. Subsequently, a solution of DenPtNPs (2 ml) was added, and the dispersions were stirred for another 2 h. Dispersions were centrifuged and precipitates were washed thoroughly and re-dispersed in water (1 ml). A dispersion (5  $\mu$ l) of synthesized electrocatalysts (GO/DenPtNPs, CNH/DenPtNPs and CNT/DenPtNPs) was drop-casted on a glassy carbon electrode (GCE, geometric surface area = 0.079 cm<sup>2</sup>) and dried at room temperature. Subsequently, nafion/ethanol solution (2  $\mu$ l, 0.5 vol%) was dropped on the electrode surface to immobilize electrocatalysts on electrode.

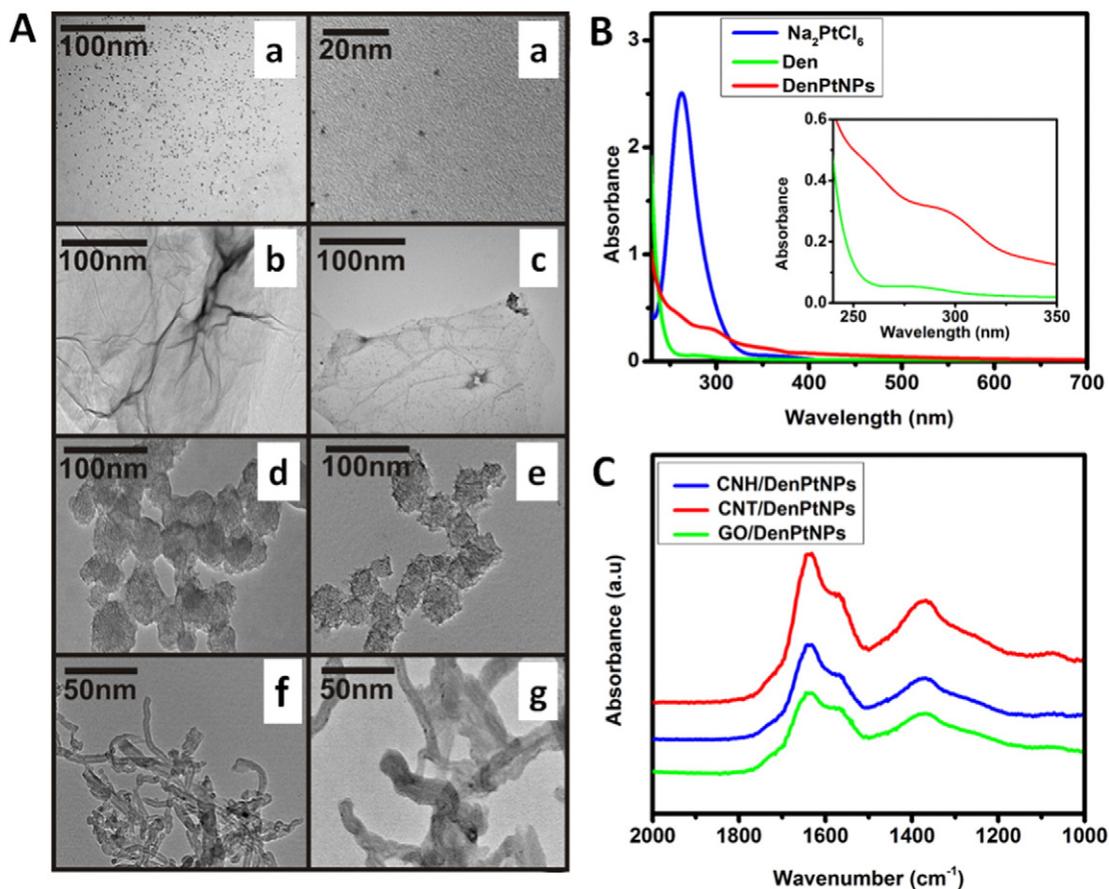
Electrochemical and impedance measurements were carried using electrocatalyst-loaded GCE, Ag/AgCl and Pt wire as working, reference and counter electrodes, respectively, on an electrochemical work station (model HZ-3000 automatic polarization system). Transmission electron microscopic (TEM) images were recorded on Hitachi H-7000 and JEM-2000 FX II. Fourier transform infrared (FT-IR) and ultraviolet (UV)-visible absorption spectroscopic measurements were performed on Nicolet 6700 and Jasco V-670 EX, respectively. A Perkin-Elmer inductively coupled plasma mass spectrometer (ICP-MS) was used to determine Pt content.

### 3. Results and discussion

PAMAM dendrimer was complexed with Pt hexachloride ions and, subsequently, the ions were reduced to zero valent state to form PtNPs encapsulated in dendrimer. Then DenPtNPs were chemically attached

on carboxyl-functionalized carbon materials through amide linkage to form carbon materials/DenPtNPs [22]. Here, the dendrimer was assigned to protect PtNPs from their aggregation. TEM morphology in Fig. 1A(a) showed that PtNPs were uniformly dispersed with an average size of  $\sim$ 5 nm. Fig. 1A(b), (d) and (f) display images of carboxyl-functionalized carbon materials, namely, exfoliated GO sheet, spherical CNH sphere and CNT tube, respectively. TEM images of corresponding DenPtNPs-immobilized carbon materials indicate that DenPtNPs were well anchored onto each carbon material and no free DenPtNPs appear on surrounding, (see Fig. 1A(c), (e) and (g)), since they were removed through the purification of crudes, even if there are. These results confirmed the strong chemical bond between DenPtNPs and carbon materials.

UV-visible absorption spectroscopic results clarified the reduction of platinum hexachloride ions: In Fig. 1B, a strong absorption band corresponding to platinum hexachloride ions was observed at 260 nm, while an amine-terminated dendrimer exhibited a weak absorption band at 282 nm (Fig. 1B(inset)) attributing to n- $\pi^*$  transition of amide group and/or amine in dendrimer [23]. After the formation of DenPtNPs, the absorption band at 260 nm was extinct but a small shoulder band at 252 nm appeared as a plasmon resonance band of PtNPs [22] with another small shoulder band at 290 nm characteristic to PAMAM dendrimer. Amide bond between DenPtNPs and carbon materials can be ascertained from FT-IR absorption spectra. While CNT showed a characteristic C=O stretching absorption band at 1765 cm<sup>-1</sup> [24], two bands, amide I and II, were located at 1645 and 1550 cm<sup>-1</sup> after the immobilization of DenPtNPs on MWCNTs, as noticed in Fig. 1C. These bands were commonly observed in composites of DenPtNPs with carbon materials. According to the results of these spectroscopies, immobilization of DenPtNPs on carbon materials was identified.



**Fig. 1.** (A) TEM images of (a) DenPtNPs, (b) GO, (c) GO/DenPtNPs, (d) CNH, (e) CNH/DenPtNPs, (f) CNT and (g) CNT/DenPtNPs. (B) UV-visible absorption spectra of Na<sub>2</sub>PtCl<sub>6</sub> precursor, PAMAM dendrimer, and DenPtNPs. (C) FT-IR absorption spectra of GO/DenPtNPs, CNH/DenPtNPs and CNT/DenPtNPs.

Fig. 2A shows electrocatalytic activities of GO/DenPtNPs-, CNH/DenPtNPs- and CNT/DenPtNPs-loaded GCE in comparison with bare- and commercial 40 wt% Pt/C-loaded GCE. Excellent HER occurred on both CNH/DenPtNPs and CNT/DenPtNPs electrodes superior to GO/DenPtNPs electrode and slightly inferior to 40 wt% Pt/C electrode, while unmodified GCE possessed poor electrocatalytic HER activity. Noticeably, less efficient HER of GO/DenPtNPs electrode than other carbon composites may be due to less graphitic domains of GO. It is the worth observation that onset potentials ( $-16$  mV) of CNH and CNT composites were close to that ( $0$  mV) of 40 wt% Pt/C electrode. Besides, at an overpotential of  $50$  mV, both CNH/DenPtNPs and CNT/DenPtNPs electrodes exhibited a current density of  $2.5$  mA/cm<sup>2</sup>, which was higher than GO/DenPtNPs electrode ( $0.4$  mA/cm<sup>2</sup>) but lower than 40 wt% Pt/C electrode ( $19$  mA/cm<sup>2</sup>). HER reaction catalyzed by individual carbon material and DenPtNPs showed extremely low current density at high overpotential alike bare electrode but unlike composites (data are not included.). Thus, the electrocatalytic activity towards excellent HER by the present composites, CNH/DenPtNPs and CNT/DenPtNPs, can be caused by following reasons;

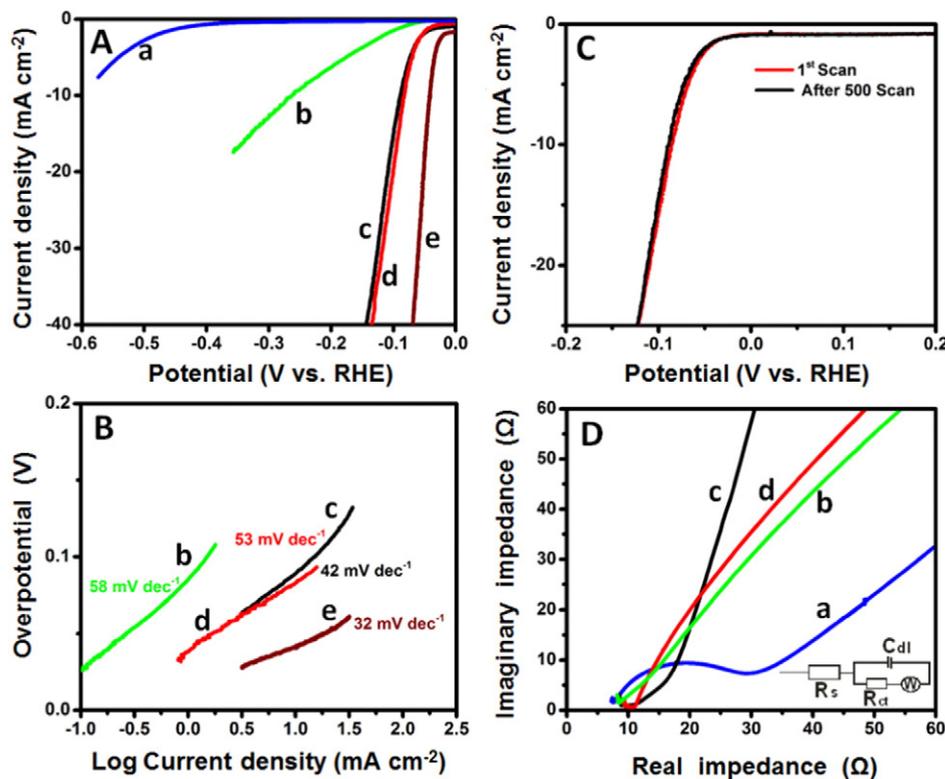
1. Highly size-controlled PtNPs stabilized by dendrimer contribute as a greatly reactive electrocatalyst, where the increased active reaction sites are provided.
2. Another significant role of PAMAM dendrimer besides stabilizer of PtNPs is a capable action as a chemical linker between PtNPs and carbon materials.
3. Of particular importance is the large graphitic domain of carbon materials. Functionalized carbon materials with electron transfer ability facilitate HER activity in addition to condensation of DenPtNPs.

In order to assess electrocatalytic activity and to elucidate reaction mechanism of electrocatalysis, a Tafel analysis is often employed [25]. Three possible reactions have generally been suggested for HER in acidic media. The first is a primary discharge step (often known as Volmer reaction), where  $\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_{\text{adsorbed}} + \text{H}_2\text{O}$ . This is followed by either

an electrochemical desorption step (Heyrovsky reaction), where  $\text{H}_{\text{adsorbed}} + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2 + \text{H}_2\text{O}$ , or a recombination step (Tafel reaction), where  $\text{H}_{\text{adsorbed}} + \text{H}_{\text{adsorbed}} \rightarrow \text{H}_2$ . Based on Tafel equation,  $\eta = a + b \log(i)$ , where  $\eta$  is the overpotential,  $i$  is the current density, and  $a$  and  $b$  are constants. Tafel slope,  $b$ , is theoretically estimated to be  $\sim 120$ ,  $\sim 40$  and  $\sim 30$  mV/decade for Volmer reaction, Heyrovsky reaction and Tafel reaction, respectively [25]. Fig. 2B shows Tafel plot of GO/DenPtNPs, CNH/DenPtNPs, CNT/DenPtNPs and 40 wt% Pt/C. The corresponding slopes were evaluated as  $58 \pm 0.35$ ,  $53 \pm 0.28$ ,  $42 \pm 0.20$  and  $32 \pm 0.15$  mV/decade, respectively, indicating the excellent HER catalytic activity. Moreover, according to theoretical Tafel slope values described above, HER on three carbon materials occurred through Volmer–Heyrovsky mechanism, different from Volmer–Tafel mechanism on 40 wt% Pt/C.

However, the Tafel slopes depend on overpotential (current density) and surface coverage. Concerning to the surface coverage, cluster expansion method has theoretically been used to simulate hydrogen adsorption isotherms and CV to identify thermodynamically stable adsorbed hydrogen configurations on PtNPs ( $< 5$  nm) surface during HER with the active species under realistic coverage, revealing that facet sites are more catalytically active than edge sites [26]. Thus, we believe that DenPtNPs ( $< 5$  nm) may exhibit similar adsorption isotherms and possess catalytically active facets than edge sites for HER.

The stability study for HER is shown in Fig. 2C. The current density and onset potential of CNH/DenPtNPs were retained even after 500 scans at the same condition. The obtained excellent durability and stability of the present electrodes should be due to the non-cleavable chemical bond between carbon materials and DenPtNPs. Besides, Nafion coating keeps the electrocatalyst film strongly on electrode surface without interruption of the HER activity of electrocatalyst. In addition, in order to ensure the electron transfer resistance ( $R_{\text{ct}}$ ) of the synthesized carbon composites, electrochemical impedance spectroscopic (EIS) analysis was performed. As shown in Fig. 2D, the bare electrode displayed the high  $R_{\text{ct}}$  value ( $\sim 28 \Omega$ ), indicating that unmodified



**Fig. 2.** Electrochemical results on (a) bare, (b) GO/DenPtNPs-, (c) CNH/DenPtNPs-, (d) CNT/DenPtNPs- and (e) 40 wt% Pt/C-modified electrodes in a  $0.5$  M  $\text{H}_2\text{SO}_4$  electrolyte solution. Scan rate:  $5$  mV/s. (A) HER polarization curves. (B) Tafel plots obtained from Fig. 2A. Numbers in figure indicate Tafel slope. (C) HER polarization curves for a CNH/DenPtNPs electrode before and after 500 scans. (D) EIS spectra. Frequency range:  $100$  mHz to  $1$  MHz; amplitude:  $5$  mV. Inset chart indicates Randles equivalent circuit used for calculating  $R_{\text{ct}}$ .

**Table 1**  
Comparison of Pt contents and HER results of present electrocatalysts to other carbon-based electrocatalysts.

Electrocatalyst	Pt content (wt%)	Onset potential (mV)	Current density	Tafel slope (mV/decade)	Reference
40 wt% Pt/C	40	0	19 mA/cm <sup>2</sup> at 50 mV	32	This work
GO/DenPtNPs	1.12	−26	0.4 mA/cm <sup>2</sup> at 50 mV	58	This work
CNH/DenPtNPs	0.86	−16	2.5 mA/cm <sup>2</sup> at 50 mV	53	
CNT/DenPtNPs	1.03	−16	2.5 mA/cm <sup>2</sup> at 50 mV	42	
Pt/MoS <sub>2</sub>	10	−	−	40	[28]
Pt/MoS <sub>2</sub> /carbon fibers	2.03	−	0.09 mA/g at 200 mV	53.6	[29]
Activated graphite rods and CNHs	−	−480	0.7 mA/cm <sup>2</sup> at 480 mV	−	[30]
MoS <sub>2</sub> /GCNT <sup>a</sup> hybrids	−	−138	10 mA/cm <sup>2</sup> at 141 mV	41	[31]
MoS <sub>2</sub> /MWCNTs	−	−90	80.3 mA/cm <sup>2</sup> at 200 mV	40	[32]
MoS <sub>2</sub> /graphene balls	−	−	−	51	[33]
MoS <sub>2</sub> /CNT-graphene	−	−35	74.25 mA/cm <sup>2</sup> at 150 mV	38	[34]
SiC-GD <sup>b</sup>	−	−8	77.4 mA/cm <sup>2</sup> at 200 mV/s	54	[35]
MoP/N,P-CNTs <sup>c</sup>	−	−	1 mA/cm <sup>2</sup> at 63 mV	51	[36]

<sup>a</sup> Graphene-carbon nanotubes.

<sup>b</sup> Graphitized nanodiamond.

<sup>c</sup> N,P-dual-doped carbon nanotube.

electrode has high electron transfer resistance. However, electrodes modified by composites of carbon materials (GO/DenPtNPs, CNH/DenPtNPs, CNT/DenPtNPs) provided  $R_{ct}$  values of 7, 12 and 14 fold, respectively, lower than that of bare electrode. These results suggest that all synthesized carbon composites have the faster electron transfer rate and in particular the CNT/DenPtNPs provided fastest electron transfer during the HER reaction in acidic condition.

An ICP-MS was employed to evaluate the accurate Pt content in the corresponding carbon material/DenPtNPs composites. Pt contents were detected as 1.12, 0.86 and 1.03 wt% for GO/DenPtNPs, CNH/DenPtNPs and CNT/DenPtNPs, respectively. Table 1 compares Pt contents and HER parameters obtained for carbon material/DenPtNPs composites to previous reports. The parameters of 40 wt% Pt/C is used as a reference for the HER efficiency of other compared materials [27]. Pt contents in carbon material/DenPtNPs composites in the present work were fairly low in comparison with Pt on MoS<sub>2</sub> and its composite. The Pt-MoS<sub>2</sub> electrocatalysts consisting of 10 and 2.03 wt% Pt exhibited the electrocatalytic activity towards HER with Tafel slope of 40 and 53.6 mV/decade, respectively [28,29]. Compared with these electrocatalysts and 40 wt% Pt/C, we achieved similar HER efficiency using only ~1 wt% of Pt content on carbon materials.

The onset potentials of HER from literatures were diverse depending on the electrocatalysts (see Table 1). The onset potential from SiC-GD was smaller than others but close to those from CNH/DenPtNPs, CNT/DenPtNPs and 40 wt% Pt/C. Since current densities in literatures were examined at different potentials, the comparison was difficult but it can be seen that current densities generally increased with increasing potential. The reported Tafel slope values in literatures were within 38–54 mV/decade, indicating the Volmer–Heyrovsky mechanism similar to that for the present carbon material/DenPtNPs electrocatalysts but being different from that for the 40 wt% Pt/C. Here, we say that this is the first report for HER using low content of Pt (~1 wt%) loaded on carbon materials but exhibiting reasonable HER efficiency comparable to that from Pt/C with 40 wt%. In other words, the present low Pt content on carbon material electrocatalysts is enough to create the HER efficiency matching commercial 40 wt% Pt/C.

#### 4. Conclusions

The low loading (~1 wt%) of Pt on composites of GO/DenPtNPs, CNH/DenPtNPs and CNT/DenPtNPs was approximately 40 times lower than commercial 40 wt% Pt/C. Nevertheless, these composites exhibit comparable HER efficiency to 40 wt% Pt/C as well as Pt/MoS<sub>2</sub>-based electrocatalysts consisting of 10 and 2.03 wt% Pt. Thus, the reported carbon-based platinum electrocatalysts have advantages of the eco-friendly and low cost synthesis procedure. Our reports clearly demonstrate

that using low weight Pt-based electrocatalyst is the auspicious route for further development of prototype hydrogen energy/battery systems.

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