Nanocomposite for methanol oxidation: synthesis and characterization of cubic Pt nanoparticles on graphene sheets

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Abstract
We present our recent results on Pt nanoparticles on graphene sheets (Pt-NPs/G), a nanocomposite prepared with microwave assistance in ionic liquid 2-hydroxyethanaminiumformate. Preparation of Pt-NPs/G was achieved without the addition of extra reductant such as hydrazine or ethylene glycol. The Pt nanoparticles on graphene have a cubic-like shape (about 60 wt\% Pt loading, Pt-NPs/G) and the particle size is \(6 \pm 3\) nm from transmission electron microscopy results. Electrochemical cyclic voltammetry studies in 0.5 M aqueous H\(_2\)SO\(_4\) were performed using Pt-NPs/G and separately, for comparison, using a commercially available electrocatalyst (60 wt\% Pt loading, Pt/C). The electrochemical surface ratio of Pt-NPs/G to Pt/C is 0.745. The results of a methanol oxidation reaction (MOR) in 0.5 M aqueous H\(_2\)SO\(_4\)+1.0 M methanol for the two samples are presented. The MOR results show that the ratios of the current density of oxidation (\(I_0\)) to the current density of reduction (\(I_b\)) are 3.49 (Pt-NPs/G) and 1.37 (Pt/C), respectively, with a preference by 2.55 times favoring Pt-NPs/G. That is, the tolerance CO poisoning of Pt-NPs/G is better than that of commercial Pt/C.

Keywords: graphene, platinum, nanocomposite, methanol oxidation, fuel cell

1. Introduction

Synthesis methods of nanocomposites for platinum on graphene have fascinated physicists, chemists and material scientists since the Nobel Laureates of physics, Geim and Novoselov, found the single-layer graphene using tape exfoliation in 2004 [1]. Graphene is one of the two-dimensional materials for the 21st century. However, because of unstable thermodynamic properties, graphene had been predicted to exist for a long time but was not actually produced until recently [2–8]. Graphene appears as a unique sp\(^2\)-bonded carbon network in single-layered structure. Possible applications of graphene are numerous. Energy is one of the fields where graphene can be utilized [9, 10]. Graphene or carbon nanotubes (CNT) may serve as a support material to anchor nanoparticle catalysts in order to improve electron transport, which provides possibilities in the design of next-generation catalysts with enhanced interactions between the substrate and the catalyst [11, 12]. Since the chemical exfoliation method can also oxidize the surface of graphene, part of the graphene structure is actually graphene oxide.
Noble metal nanoparticles have been decorated on carbon materials for use in direct methanol fuel cell (DMFC) applications ever since nanotechnology was in its developing stage. The carbon materials for DMFC or proton exchange membrane fuel cell application usually possess high specific surface area, electrical conductivity, chemical stability and so on [11–13]. The commonly used carbon materials for DMFC are active carbon, Vulcan XC-72 carbon black, multi-walled/single-walled CNT and graphene (such as graphene oxide or functionalized graphene) [14–16]. In order to improve the solubility of carbon materials in fuel cell applications, sulfonation was applied to CNT, carbon black or active carbon for better solubility prior to making the devices. In this study, the graphene layers were also sulfonated to give better water affinity [17, 18].

Since the expensive Pt is the best transition metal for fuel cell technology, its electrocatalytical efficiency should be balanced with its cost in fabrication. The well-dispersed nanoparticles, Pt or Pt–M alloys (M for Ru, etc), on electrodes are the desirable conditions in practice [19–22]. A lower Pt loading with a higher electrocatalytical property is the optimum goal. Herein the synthesis of graphene materials follows the procedures outlined below: (i) strong oxidation of graphite to produce graphite oxide (GO), (ii) surface modification of GO with simultaneous reduction of GO to graphene and (iii) reduction reaction for the precursors of noble metal ions (and simultaneously for GO) to become nanoparticles on graphene sheets. The cubic Pt nanoparticles were usually synthesized with reducing agents and surfactants, such as citrate and oleic acid or polyvinylpyrrolidone [23–26]. One possible barrier for the Pt electrode in the DMFC application is its CO poisoning. CO is constantly present during the methanol oxidation reaction in that CO likely occupies the active sites on the Pt electrode, drastically reducing the activity [27–29].

Ionic liquids, as green chemicals for use in environmentally friendly synthesis, have enhanced physical properties suitable for replacing common organic solvents, especially the ones used at high temperatures. The advantages of ionic liquids are (a) almost no vapor pressure, (b) a much greater temperature range as a liquid and (c) varying solubility for organics, inorganics and polymers. Ionic liquids have found numerous uses as reaction and extraction media [30–32].

The 2-hydroxyethanaminium formate was introduced by Bicak et al in 2005 [33]. Later, Mudring et al synthesized porous silver materials using 2-hydroxyethanaminium formate with microwave assistance [34]. Without an extra reducing agent, the Ag⁺ salt was reduced by the ionic liquid itself. With liberation of carbon dioxide, the formate solid was known to produce hydrogen that reduces the Ag⁺ into Ag⁰. Taking this precedent example as a model synthesis, we have succeeded in the preparation of cubic Pt nanoparticles on graphene sheets (Pt-NPs/G) using this simple 2-hydroxyethanaminium formate as a reactive solvent with microwave assistance.

Herein, we describe the synthesis of cubic Pt-NPs/G nanocomposites for methanol oxidation reaction (MOR) application to compare with a commercial one having a similar electrocatalyst weight loading of about 60 wt%. The green chemical synthesis method employed the ionic liquid that was acting as the medium and as the reducing agent. The resistance to CO-poisoning of the electrocatalytical nanocomposites reported in this study was better than that of commercial ones as evidenced in the MOR faradic current density ratios (vide infra).

2. Experimental

2.1. Modified graphene sheets

The graphene synthesis followed a modified Hummer’s method [31]. Concentrated sulfuric acid (25 ml) was poured into a 250 ml round-bottomed flask held in an ice bath. Then fumed nitric acid (10 ml) was added slowly in 15 min. Graphite powder (1 g) was introduced under vigorous stirring into the flask kept in the ice bath. After being mixed well, the solution was added with potassium chlorate (22 g) in 30 min. The ice bath was removed and the solution was stirred at room temperature for 96 h. Suitable amounts of deionized (DI) water were added to the product mixture kept in the ice bath and the solution was centrifuged for removal of the liquid phase. The procedure was performed three times. The solids collected were rinsed with methanol three times. The mud-like solid was dried at 80 °C for 12 h to yield the GO.

Sulfonation of GO was carried out using the following procedure: 250 mg graphite oxide in 250 ml DI water was stirred for 30 min before the addition of 1.4 g NaBH₄, and kept at 80 °C for 1 h. After centrifugation, the mud-like residuals were rinsed with methanol three times and then dried at 80 °C in an N₂ atmosphere for 1 h. After being dried, the mixture of the above residuals (158 mg) in 300 ml DI water was dispersed in a round-bottomed flask for 30 min using an ultrasonic bath. Sulfanilic acid (140 mg) together with potassium nitrate (50 mg) was introduced into a 100 ml beaker containing DI water (40 ml), employing an ice bath. After being mixed well, 1 N HCl (1 ml) was added to the solution and then the solution was poured into the round-bottomed flask and stirred for 2 h in the ice bath. Centrifugation followed by removal of aqueous solution resulted in the sulfonated graphene, which was rinsed with methanol a few times and then dried at 80 °C in an N₂ atmosphere.

The microwave-assisted synthesis of the Pt-NPs/G composite was performed using a CEM Discover Du7046 microwave set with 20 W power output for 30 s to increase the temperature to 80 °C and then held at 80 °C for 5 min. Three samples were prepared with graphene or sulfonated graphene (100 mg) as substrates and with grinded K₂PtCl₆ at 355, 355 or 100 mg, respectively, plus 2-hydroxyethanaminium formate (5 g), in Pyrex glass tubes. The cubic Pt-NPs/G was the one with the K₂PtCl₆/sulfonated graphene w/w ratio of 3.55. The preparation of 2-hydroxyethanaminium formate (shown in scheme 1) was done by a slow neutralization of H₂NCH₂CH₃OH (20 ml) and formic acid (14 ml) in a 100 ml round-bottomed flask kept in the ice bath.
2.2. XRD characterization

Cubic Pt-NPs/G crystalline materials mixed with estimated 1 wt% graphite were examined using the PANalytical X’Pert Pro MPD powder x-ray diffractometer (XRD) with Cu Kα radiation at 50 kV and 40 mA. The scanning rate was 0.625° min\(^{-1}\) and the 2θ range was 5–80°.

2.3. Fourier transform infrared (FT-IR) characterization

The samples for FT-IR analysis consisted of composite materials (5 mg) with dried KBr (100 mg), well mixed and ground and then pressed into pellets for measurement. The Perkin Elmer spectrum 100 FT-IR was scanned from 400 to 4000 cm\(^{-1}\), signals being accumulated 32 times and resolution about 0.01 cm\(^{-1}\).

2.4. Pt content measurement with thermal gravimetric analysis and inductively coupled plasma mass spectrometry (ICP-MS)

Thermal gravimetric analysis (TGA) was performed using the Perkin Elmer Pyris 1 TGA (the resolution was about 0.1 μg) with about 5 mg sample loading on the platinum plate, from room temperature to 900°C at a heating rate of 5°C min\(^{-1}\). The Pt content was measured alternatively using an Agilent 7700 Series ICP-MS.

2.5. Transmission electron microscopy (TEM) characterization

The TEM analysis was performed on a JEOL 2010FX with a LaB\(_6\) electron gun operated at 200 kV. The TEM samples were prepared with ethanol dispersion dropped on the grid Cu net for analysis. The selected area electron diffraction (SAED) was employed to reveal the cubic Pt-NPs/G electronic diffraction pattern and the lattice distances (d-spacing).

2.6. X-ray photoelectron spectroscopic (XPS) analysis

A Physical Electronics PHI Quantra XPS microprobe equipped with an Al Kα monochromatic x-ray source (1486.6 eV, 45° incident angle) was employed on the cubic Pt-NPs/G and the commercial Pt/C samples.

2.7. Electrochemical analysis

Cyclic voltammetry (CV) was employed with the conventional three-electrode glass cell Radiometer Voltalab 40 at room temperature. The glass-carbon working electrode was pre-polished, and then alcohol immersed. The working electrode was surface covered with 20 μL dispersions of cubic Pt-NPs/G (13.75 μg cm\(^{-2}\)) or alternatively that of Pt/C (17.50 μg cm\(^{-2}\)), which was the commercial 60 wt% Pt (Uni

![Figure 1. FT-IR spectra of GE, GO-SO\(_3\)H and GO.](image-url)

Ward Co. Ltd, Taiwan). The reference electrode was Ag/AgCl and the counterelectrode was a Pt wire. The electrochemical surface area (ECSA) was evaluated in 0.5 M aqueous H\(_2\)SO\(_4\) and the scanned voltage from −0.2 to 1.2 V with a scan rate at 20 mV s\(^{-1}\). The methanol oxidation was measured at 20 mV s\(^{-1}\) scan rate from 0 to 1.0 V in 0.5 M aqueous H\(_2\)SO\(_4\) + 1 M aqueous methanol.

3. Results and discussions

3.1. Synthesis and characterization of cubic Pt-NPs/G

The results of chemical exfoliated reaction are shown in figure 1 with the FT-IR spectra for graphene (GE), sulfonated graphite oxide (GO-SO\(_3\)H) and graphene oxide (GO). The assignments of the peaks on GO were 1715 cm\(^{-1}\) for –OH bonds. There were weak peaks for C–O bonds around 1100–1300 cm\(^{-1}\), signals being accumulated 32 times and resolution about 0.01 cm\(^{-1}\). The assignments of peaks on GO-SO\(_3\)H for the C–O bonding mode. The broad peaks for N–H bonds, 2359 cm\(^{-1}\), signals being accumulated 32 times and resolution about 0.01 cm\(^{-1}\). The assignments of peaks on GO-SO\(_3\)H were 1750 cm\(^{-1}\) for N–H bonds, 2359 cm\(^{-1}\) for nitrile, 1696 cm\(^{-1}\) for C–N–C vibration modes, 1260–1210 cm\(^{-1}\) for the C–O–C mode and 1053 cm\(^{-1}\) for C–O bonds.

The three cubic Pt-NPs/G composites were different in w/w ratios of sulfonated graphene/K\(_2\)PtCl\(_6\) or GO-SO\(_3\)H/K\(_2\)PtCl\(_6\) at 1/3.35, 1/3.35 and 1/1 in the preparation. Only the ones with the w/w ratio of sulfonated graphene/K\(_2\)PtCl\(_6\) at 1/3.35 yielded the cubic Pt-NPs/G composite with particle size at 6 ± 3 nm and Pt loading.
was estimated to be at 62.83 wt% by the TGA examination (shown in figure 3(a)) and at about 61.82 wt% by the ICP-MS measurement. The same ratio at 1/3.35 for GO-SO$_3$H/K$_2$PtCl$_6$ produced cubic Pt-NPs/GO with about 40.08 wt% Pt loading and an average particle size of 18 ± 5 nm. The surface oxygenated functional groups had affected apparently the nucleation on nanoparticle synthesis. If the ratio was lowered to 1/1 for GO-SO$_3$H/K$_2$PtCl$_6$, the Pt-NPs/GO formed exhibited a smaller average particle size. Figure 2 shows the TEM results and the particle size distribution of Pt nanoparticles on cubic Pt-NPs/G composite.

Table 1 reveals the results of sulfonated graphene/K$_2$PtCl$_6$ and graphene oxide/K$_2$PtCl$_6$ in different w/w ratios. There was no extra reducing agent employed during the synthesis, the ionic liquid 2-hydroxyethanaminium formate also playing the role of a reducing agent.

The ionic liquid 2-hydroxyethanaminium formate was utilized by Mudring et al in the synthesis of the monolith silver, a porous material, together with the microwave heating technique without the addition of an extra reducing agent. Ag$^+$ was reduced from Ag$^{3+}$. Mudring had observed the formation of CO$_2$ gas in the synthesis with the above-mentioned ionic liquid. We believe that the current formation of Pt$^0$

Table 1. Synthesis of Pt-NPs/G with 2-hydroxyethanaminium formate ionic liquid with microwave assistance.

| Loading (mg) | K$_2$PtCl$_6$ | Ionic liquid | Substrate$^b$ (100 mg) | Shape/size (nm) |
|-------------|---------------|--------------|------------------------|-----------------|
| 1           | 355           | 15 000       | GE                     | Cubic/6 ± 3     |
| 2           | 355           | 15 000       | GO                     | Cubic/18 ± 5    |
| 3           | 100           | 15 000       | GO                     | Spheric/14 ± 4  |

$^a$ 20 W power output for 30 s and then the reaction vessel was kept at 80 °C for 5 min.

$^b$ Sulfonated substrates.

Scheme 2. The proposed reduction mechanism of 2-hydroxyethanaminium formate.

nanoparticles proceeds in a similar way. The Pt$^{4+}$ metal ions were reduced to Pt$^0$ at the expense of the formate that was concurrently oxidized to CO$_2$. Scheme 2 shows the possible redox pathway, parallel to the findings of Mudring and co-workers [34].
The TEM analysis gives images of (1) reveals the two peaks assigned to Pt 4f and table. Figure / to Pt precursors in a w/w ratio of 1 cubic Pt-NPs/G started initially from sulfonated graphene. As shown in figure / that the Pt loading of cubic Pt-NPs/G was about 61.83%. The ICP-MS result indicated and 12.78 wt%, respectively. The XRD diffractogram was recorded on the synthesized samples and (b) XRD diffractogram of cubic Pt-NPs/G TGA results for estimating Pt contents of the three samples, as calculated using the equation (about 382–383 eV) and C–OH values of 25, 46.3° and 67.8°, respectively. The metallic state Pt is more associated with methanol oxidation and electrochemical activity [35, 36].

The amount of Pt nanoparticles on Pt-NPs/G composite was measured with TGA. The Pt loadings on samples in table 1, entries 1–3, were estimated to be about 62.83, 40.08 and 12.78 wt%, respectively. The Pt nanoparticles produced with the ionic liquid 2-hydroxyethanaminium formate with microwave assistance are not different from the Pt nanoparticles produced commercially. The Pt species in cubic Pt-NPs/G and that in Pt/C are 44.4 and 45.56%, respectively. The Pt catalyst has very similar environments. The results suggest that the cubic Pt-NPs/G and Pt/C have very similar environments. The sp2–C–C percentage of the cubic Pt-NPs/G is estimated to be 42.42% and that of the commercial Pt/C 48.02%. The carbon black is generally made by the high-temperature sintering method so that the electrical conductivity is suitable for fuel cell catalyst support in terms of enhanced catalytic activity and corrosion resistance. The corrosion behavior might affect the performance and stability of the Pt catalyst [37]. The oxygenated functional groups on the surface are further divided into hydroxyl and epoxy groups (from C1s XPS narrow band spectrum data analysis), totaling 57.58% on the cubic Pt-NPs/G (C–OH group for 27.29%, and C–O–C group for 30.29%) and 51.93% on Pt/C (C–OH group for 27.29%, and C–O–C 28.66%). O 1s XPS spectra were shown in figures 4(e) and (f). Both cubic Pt-NPs/G and Pt/C spectra were fitted to the three peaks as phenol (about 384 eV), C–OH (about 382–383 eV) and C = O (about 381 eV). The C–OH ratio of cubic Pt-NPs/G was larger than the Pt/C, suggesting in part more anti-CO-poisoning of the cubic Pt-NPs/G (see figure 4 and table 2).

3.2. ECSA analysis

The CV analysis for ECSA was measured in 0.5 M aqueous H2SO4 at 20 mV s−1 scan rate from −0.2 to 1.2 V versus the Ag/AgCl reference electrode. For comparison the CV results of two Pt-containing electrocatalysts were stacked in figure 5. In the range −0.2 to 0.1 V (versus Ag/AgCl) in potential, the marked areas (in black and red dashed lines) are the ECSA for the two samples, as calculated using the equation

\[
\text{ECSA} = Q_H \mu \text{C cm}^{-2}/(210 \mu \text{C cm}^{-2} \times \text{Pt} \mu \text{C cm}^{-2}),
\]
Figure 4. XPS spectra of cubic NPs/G and Pt/C composites: (a) Pt 4f XPS of cubic Pt-NPs/G, (b) Pt 4f XPS of Pt/C, (c) C 1s XPS of cubic Pt-NPs/G, (d) C 1s XPS of Pt/C, (e) O 1s XPS for Pt-NPs/G and (f) O 1s XPS for Pt/C.

Table 2. XPS peak position and percentage contributions of cubic Pt-NPs/G and Pt/C.

|                  | Pt $4f_{7/2}$ | Pt $4f_{5/2}$ | C 1s | O 1s |
|------------------|--------------|--------------|------|------|
|                  | Pt$^{0}$     | Pt$^{2+}$    | Pt$^{4+}$ | sp$^{2}$ | C–OH | C–O–C | >C=O | C–OH | Phenol |
| Cubic Pt-NPs/G (eV) | 70.6         | 71.3         | 72.6   | 74.3   | 75.3   | 75.9   | 284.0 | 285.1 | 286.2 | 531.2 | 532.2 | 534.8 |
| %                | 24.4         | 11.9         | 9.2    | 20.0   | 18.9   | 15.9   | 42.4  | 27.3  | 30.3  | 14.2  | 55.3  | 30.5  |
| Pt/C (eV)        | 70.7         | 71.5         | 72.4   | 74.2   | 75.2   | 76.1   | 283.8 | 285.2 | 286.1 | 529.8 | 531.7 | 533.6 |
| %                | 23.3         | 12.6         | 6.4    | 22.2   | 16.4   | 19.1   | 48.7  | 23.3  | 28.7  | 19.9  | 48.3  | 31.8  |
where $Q_H$ ($\mu$C cm$^{-2}$) presents the value of hydrogen adsorption of the Pt active sites on the surface. The constant 210 is the charge required to oxidize a monolayer of $H_2$ on the single-crystal Pt surface. The Pt loading is presented in $\mu$g cm$^{-2}$. The ECSA result for cubic Pt-NPs/G was 24.16 m$^2$ g$^{-1}$ and that of the commercial Pt/C was 32.45 m$^2$ g$^{-1}$. The ratio of Pt-NPs/G to commercial Pt/C was 0.745. The ECSA of commercial Pt/C is greater than that of cubic Pt-NPs/G.

### 3.3. Methanol oxidation reaction

The MOR was measured in 0.5 M aqueous $H_2SO_4 + 1.0$ M aqueous $CH_3OH$ at a scan rate of 20 mV s$^{-1}$, with electrocatalysts as the glass-carbon working electrode and a Pt wire as the counterelectrode. The loading of cubic Pt-NPs/G was 13.75 $\mu$g cm$^{-2}$ and that of Pt/C was 17.50 $\mu$g cm$^{-2}$.

The current densities, normalized by glass-carbon area, are shown in figure 6(a). The forward faradic anodic peak at about 0.6–0.9 V versus Ag/AgCl was identified as $I_f$ (methanol oxidation) and the backward faradic scanning peak at about 0.2–0.7 V versus Ag/AgCl was identified as $I_b$ (CO additive formation on the Pt electrocatalyst surface). The onset potentials of $I_f$ were 0.28 and 0.20 V for cubic Pt-NPs/G and Pt/C, respectively. The forward anodic maximum peak potentials of methanol oxidation were assigned at 0.70 and 0.74 V versus Ag/AgCl for the cubic Pt-NPs/G and Pt/C, respectively. The backward scan maximum peak potentials were 0.53 and 0.5 V versus Ag/AgCl for the cubic Pt-NPs/G and the Pt/C, respectively. The difference of methanol oxidation peak potentials was highly correlated with the oxygenated functional groups on the surfaces of the graphene sheets or of the carbon black. Overall, the $I_f/I_b$ ratios implied the CO-poisoning attribution of the electrocatalysts [19, 27].

Figure 6(a) shows that the methanol oxidation ability follows the ECSA results of the cubic Pt-NPs/G and of the Pt/C. The $I_f/I_b$ ratios were in reversed order: 3.49 for the cubic Pt-NPs/G and 1.37 for the Pt/C. The $I_f$ of Pt/C to the $I_f$ of cubic Pt-NPs/G was 2.39 times greater and the $I_b$ of Pt/C to the $I_b$ of cubic Pt-NPs/G was 6.1 times greater. Thus, the CO additive formation on the Pt/C modified working electrode ought to be much faster than that on the cubic Pt-NPs/G modified working electrode. It would be problematic in long-term application of methanol oxidation if the active sites of oxidation are occupied by CO.

The current densities, normalized by Pt loading weight, are shown in figure 6(b). The methanol oxidation CV suggests that the current density per mg of cubic Pt-NPs/G is better than that of Pt/C. The $I_f$ ratio (cubic Pt-NPs/G to Pt/C) was 0.53 and the $I_b$ ratio was 0.21 (cubic Pt-NPs/G to Pt/C). Based on ECSA results the ratio of electrocatalyst active sites between cubic Pt-NPs/G and Pt/C was 0.745. Based on MOR results the ratios of $I_f$ and $I_b$ were both lower than 0.745. However, figure 6(b) indicates that the $I_f$ peak height of cubic Pt-NPs/G is greater than that of Pt/C; in other words, the cubic Pt-NPs/G has a higher CO tolerance.

Given in figure 7(a) is the larger aggregation morphology for the commercial Pt/C. Figures 7(b) and (c) are higher-magnification images for the aggregation morphology and SAED pattern of the same Pt/C. A lower magnification image is shown for comparison with the similar magnification image of cubic Pt-NPs/G in figure 2(a). The well-dispersed Pt particles on the graphene sheets were apparently more preferred than that of Pt/C. The SAED pattern exhibits a $d$-spacing of about 0.23 nm. The aggregation surely reduces the active areas for electrocatalysis and hence the catalytic activity decreases.
With cubic Pt nanoparticles anchored on the surface of graphene sheets, the ECSA and MOR results suggest that the advantages of the cubic Pt-NPs/G composite may likely lie in the CO-antipoisoning aspect.

4. Conclusions

In this study, we produced the cubic Pt nanoparticle decorated graphene sheets (cubic Pt-NPs/G) in ionic liquid 2-hydroxyethanaminium formate with microwave assistance. The ratio of sulfonated graphene to the Pt precursor is 1/3.55 for better dispersion in aqueous solutions, resulting in the cubic Pt-NPs/G nanocomposite. There is neither hydrazine nor ethylene glycol serving as the added reductant to convert the Pt precursor to Pt nanoparticles. The Pt loading of cubic Pt-NPs/G is 60% by weight from the TGA results. The Pt crystallites of cubic Pt-NPs/G were in an fcc structure and the Pt particle sizes were about 5–10 from TEM and SAED results. The ECSA of cubic Pt-NPs/G is smaller than that of commercial Pt/C. So is the MOR ability. The ECSA for cubic Pt-NPs/G and that for Pt/C are 24.16 and 32.45 m² g⁻¹, respectively, whereas the MOR I₁/I₂ ratio for cubic Pt-NPs/G and that for Pt/C are 3.49 and 1.37, respectively. A high MOR I₁/I₂ ratio indicates that cubic Pt-NPs/G as the electrocatalyst is the better one for long-term fuel cell applications.

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Figure 7. TEM images of commercial Pt/C aggregation morphologies: (a) low-magnification image, (b) SAED pattern and (c) high-magnification image of (a).