In Situ Construction of Small Pt NPs Embedded in 3D Spherical Porous Carbon as an Electrocatalyst for Liquid Fuel Oxidation with High Performance

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1. Introduction

Fuel cells (FCs) have been considered for a long time as a nonpolluting and efficient power generator for substitution of fossil energies. Especially, low-temperature direct alkaline alcohol FCs (DAAFCs) have been attracting increasing attention for practical utilizations to date because of their portability as serving effective power sources. However, compared with common DAAFCs using methanol and/or ethanol as fuel sources, direct ethylene glycol FCs exhibit some more evident advantages, for instance, lower toxicity, higher boiling points, and higher theoretical energy density with fewer regulation violations, making them more practicable to work with. So far, many efforts have been made to develop various anode electrocatalysts for DAAFCs, typically as demonstrated in ethylene glycol oxidation reactions (EGORs). In such demonstrated cases, elemental platinum (Pt) is still the key component for the catalysis of DAAFCs, and many more catalytic reactions have been applied to the applications of FCs theoretically and technically. For example, there have been excellent demonstrations of catalysis over various Pt and Pt-based nanostructures including hollow nanoframes, core@shell nanostructures, and nanodendrites with reduced sizes but the increased surface area enhanced both specific and mass activities. These optimized designs over Pt or Pt-based catalysts would be available for FC utilizations commercially. However, some intermediates, especially CO generated from EGORs, will poison the Pt-based catalysts and further weaken their stability. Therefore, there still remains an enormous challenge to study DAAFCs with a well-developed anode for the electrocatalytic oxidation of liquid fuels actively, feasibly, and stably.

Compared to the bulk counterpart, the supporting strategy is actually a powerful profile to improve the catalytic performances of the nanostructured Pt-based composites. In addition to typical oxide-type catalyst supports of titania, indium tin oxide, tin oxide, alumina, silica, and tungsten oxide, carbonaceous supports including graphene, conducting polymers, carbon nanotube, and nanoporous carbon have been proved to be a kind of effective and compatible ones for the Pt/Pt-based nanostructured catalysts based on intensive investigations. Generally, the synthesis of these supported metal catalysts commonly involves multistep processes of preparing initial protected Pt/Pt-based nanoparticles (NPs), loading on appropriate supports mechanically and activating the NPs to expose active sites. The procedure is complicated in general and the catalytic activity fades out commonly because...
of the loss of active components from the supports in catalysis process. As a comparison, a one-pot in situ preparation of metal NPs directly dispersed on the catalyst support of conductive carbon would be much more convenient and powerful to optimize the electrocatalysts probably with self-sustained nanostructures possessing an improved functionality and performance. Furthermore, a supported carbon would limit the detachment, migration, and agglomeration of these active metallic NPs, thus enhancing the durability of catalysts in FCs. However, the catalytic performance may be lowered when the catalyst is covered with a very thick carbon shell. Therefore, it will be very important and challenging to appropriately limit the size of the active nanostructures and acquire a thin carbon conductive shell for improving the activity and durability of the catalyst.

To achieve this goal, in the present work, we develop a mild and facile profile for the synthesis of very small sized Pt NPs that would be in situ embedded in conductive three-dimensional (3D) spherical porous carbon (shortened as the 3D Pt/C composite) generated in the synthetic process. Compared to the commercial catalyst of Pt black, the 3D Pt/C composite demonstrates well-improved electrocatalytic performance for EGORs as well as for ethanol oxidation reaction (EOR) and methanol oxidation reaction (MOR).

The 3D Pt/C composite electrocatalyst was readily prepared in the route, as schematically depicted in Scheme 1. Typically, the first synthesized precursor of the uniform spheres was annealed to transform into an in situ formed 3D Pt/C composite catalyst.

Scheme 1. Fabrication Scheme for 3D Pt/C Composite

| PtCl₂ | NO₂⁻ | Pt²⁺ complex |
|-------|------|--------------|
| NH₄OH | Pt²⁺ complex |

![Fabrication Scheme for 3D Pt/C Composite](image)

2. RESULTS AND DISCUSSION

The 3D Pt/C composite fabricated in the current synthetic process has been identified by powder X-ray diffraction (XRD). It is found that there are four major diffraction peaks of the 3D Pt/C composite located at 40.10°, 46.49°, 67.78°, and 81.44° (2θ) that can be well indexed to the facets of face-centered cubic (fcc) Pt (111), (200), (220), and (311), respectively (JCPDS 00-001-1194), as displayed in Figure 1a. The Pt nanocrystals (NCs) in the 3D Pt/C composite have an average grain size (about 4.0 nm) according to the calculation of (111) plane diffraction over Scherrer’s equation. The chemical states and compositions of the 3D Pt/C composite were determined using X-ray photoelectron spectroscopy (XPS). In the survey spectrum, only Pt, C, and O are obviously observed while the N signal is not so clear to be detected in the spectrum (Figure S1a). In the Pt close-up spectrum (Figure 1b), two distinct peaks of 4f⁷/₂ (71.6 eV) and 4f⁵/₂ (74.9 eV) for Pt(0) can be well indexed. The broadened and intensive binding energy centered at ~284.8 eV is attributed to graphite-like carbon in addition to contaminant carbon (Figure S1b). The existence of O (Figure S1c) is commonly resulted from oxygen adsorption onto the sample, whereas the N signal is relatively weak as seen in the close-up spectrum (Figure S1d). The N signal is detected to be oxidized N (405.5 eV and 402.2 eV) in addition to pyridinic N (399.5 eV) and pyridinic N (398.3 eV). The investigations manifest that the fabricated composite is composed of fcc Pt NCs embedded in carbon with trace nitrogen. However, Raman spectrum (Figure 1c) suggests that the generated carbon is not well crystallized in the sample because the vibration at 1343 cm⁻¹ (D-band) is so intense as compared to that at 1597 cm⁻¹ (G-band). Meanwhile, as shown in Figure 1d, the typical overall Pt loading in the product was determined by air atmosphere thermogravimetric analysis (TGA) and the specific value was 45.54%. XRD detection shows that only pure Pt remained in the sample after the air atmosphere TGA (Figure S2), and it is a convincing detection of Pt content via TGA.

The fabricated 3D Pt/C sample was also studied by transmission electron microscopy (TEM), scanning electron microscopy (SEM), high-resolution TEM (HR-TEM), and selected area electron diffraction (SAED). From Figures 2a and S3, it is observed that the 3D Pt/C composite is composed of uniform nanostructured spheres and their average size is ~206.8 nm, as appeared in the corresponding size distribution histogram (Figure S4). Both low- and high-magnification TEM images confirm that the 3D Pt/C composite has uniform nanospheres which are composed of numerous minute Pt NPs dispersed well in the spherical carbon matrix without any obvious aggregation (Figure 2b–e). In detail, as seen in Figures 2d and S5, the Pt NPs are approximately 4.4 nm in size (Figure 2d), which agreed to the calculated data from Scherrer’s equation over XRD detection (Figure 1a), and the shell thickness of carbon matrix/coating is approximately 1.66 nm (Figure 2e). In the HR-TEM image (Figure 2f), an
interfringe distance of 2.25 Å is observed, close to d-spacing of the (111) lattice plane in metallic Pt NCs. The corresponding SAED pattern further confirmed the structure of the polycrystalline Pt NPs in the composite (inset in Figure 2f). Meanwhile, a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of the 3D Pt/C composite (Figure 2g) and its corresponding elemental mappings including electron energy loss spectroscopy (EELS) mappings (Figure 2h) and energy-dispersive X-ray spectroscopy (EDX) (Figure 2i) were performed in the work. The C element (red in Figure 2h) in addition to Pt (Figure 2i) is uniformly distributed in the whole spherical sample (Figure S6) with different densities. Both C and Pt mappings are close to detection by TEM (Figure 2b–f). These results reveal that ultrathin carbon coating and homogenous carbon are distributed within the 3D Pt/C composite, which can prevent the immigration and agglomeration of the Pt NPs generated in the preparation and annealing treatment. The microstructure of the 3D Pt/C composite is revealed by using N₂ adsorption–desorption isotherm. From isotherm plot, the Brunauer–Emmett–Teller (BET) surface is calculated to be as high as 139.342 m² g⁻¹. Meanwhile, the total pore volume of the composite is determined to be about 0.1768 cm³ g⁻¹ and the micropore volume is 0.067 cm³ g⁻¹. It is detected that the 3D Pt/C composite shows microporous and mesoporous feature with 5.133 nm in average pore diameter (Figure S7). The 3D Pt/C composite with relatively high surface area in addition to the manifold pore diameter would be favorable for the enhancement of electrocatalytic performance since the electrolyte can penetrate completely into the pores, leading to a higher electrode/electrolyte contact area.40

In the present synthetic protocol, the 3D Pt/C composite is pyrolytically derived from a complex precursor of highly uniform nanospheres prepared hydrothermally in the media of deionized water with toluene (PhCH₃). As seen in SEM image (Figure S8a), the spheres of the complex precursor are of highly uniform and monodisperse (~269.0 nm) calculated from the corresponding size distribution histogram (Figure S8b). Low- and high-magnified TEM images confirmed the complex precursor spheres in high quality (Figure S8c,d). The diameter of the precursor spheres is nearly 30% larger compared to the annealed 3D Pt/C composite, demonstrating that an obvious shrinkage occurs during the annealing process.40 XRD detection suggests that the complex precursor spheres are not well crystallized in the hydrothermal process because there are only some very weak diffraction peaks observed in the range of 30°–65° (2θ) in the pattern (Figure S9a) due to a very small amount of Pt(0) nanocrystallites and possible oxide impurity produced in very small size mixed with the organic complex (Figure S9b). In the XPS spectra of the spherical precursor (Figure S10), elemental Pt, C, N, O, and Cl species are easily revealed, and the oxidation state of Pt is mainly Pt(II) species besides a very small percentage of Pt(0). Compared with the complex precursor (Figure S8), the elements of N and Cl in the annealed sample are not easily observed in the survey XPS spectrum (red circles in Figure S1a) due to the flow of Ar/H₂ even though there is trace N doped in the 3D Pt/C composite in high-resolution N 1s XPS spectrum (Figure S1d). In addition, it is found that there are only monodispersed Pt NPs obtained without addition of 4-nitrophenol in the synthetic system (Figure S11), which suggests that the employment of 4-nitrophenol plays an important role in the formation of the spherical precursor complex (Figures S8 and S9). To obtain the 3D Pt/C composite with well-dispersed Pt NPs, we try to prolong the reaction time (up to 20 h), and it is found that there are some more elemental Pt NCs detected in the product based on XPS, XRD, and TEM determinations (Figures S12 and S13). It is concluded that long reaction time is favorable for the reduction of Pt(II) species to Pt NCs kinetically in outer surface from the spherically polymeric complex of Pt(II) source with 4-nitrophenol (Figure S9).

The solvents could also influence the morphologies of the products at the same time as they are varied when the mixed solvent of H₂O with toluene (PhCH₃) was replaced completely by deionized H₂O (removing toluene) in the reaction system (Scheme 2). In detail, the product was identified as Pt@4-nitrophenol core@shell nanostructures (Figure S14), in which

![Figure 2](https://example.com/image.png)

**Figure 2.** (a) SEM, (b,c) low- and high-magnification TEM images for the 3D Pt/C composite, (d) corresponding Pt NP size distribution histogram, (e,f) HR-TEM images with inserted SAED (inset in f), and (g–i) HAADF-STEM with EELS mapping for C and EDX mapping for Pt of the as-synthesized 3D Pt/C composite.

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**Scheme 2.** Schematic Illustration for the Product with Different Morphologies Produced in Two Different Media of PhCH₃/H₂O and H₂O Hydrothermally

![Scheme 2](https://example.com/scheme.png)
the shells were determined to be 4-nitrophenol by 1H nuclear magnetic resonance (NMR, Figure S15). When a mixture of toluene and water was served as the solvent, the target product of spheres can be prepared using an optimal proportion of toluene and water as 1:1. The morphology is uniform and excellent enough for serving as the precursor in the following annealing process. When some other organic solvents, for instance, cyclohexane, chloroform, and ethanol, were introduced to mix with water as solvents, however, we could not obtain the 3D Pt/C composite except for core@shell structured or metal NPs with different sizes (Figure S16). Experimental investigations suggest that toluene with water was favorable for the formation of the complex sample in spherical shapes probably because of an interaction of the two-phase flow thermodynamically in the solvothermal process.41

In the current work, the two-phase system with both hydrophilic and hydrophobic solvents of immiscible water and toluene with the optimal given ratio tend to be a kind of microemulsions42 or a microemulsion-like situation at temperatures higher than their boiling points under the solvothermal conditions even though there are not any surfactants involved in the solvothermal system. It is understood that the microemulsion-like situation would be favorable for the formation of monodispersed and uniform spherical precursors at elevated temperatures over boiling points as the mixtures of toluene and water were served as the solvents in the present solvothermal system because spherical geometry has a reduced surface energy at the same time in thermodynamics. However, it is also noted that there are still some small thin plate-like shapes found on the outside of the spherical precursors, especially at early reaction stage, as seen in the low- and high-magnified SEM images in Figure S17. The result suggests that the self-assembly spherical samples generated in the present microemulsion-like situation induced by the solvothermal treatment have still some difference (with less stability) from those formed in a typical microemulsion with an assistance of surfactant molecules forming a monolayer in interface between water phase and toluene as oil phase.42

The electrocatalytic performance toward EGOR, MOR, and EOR was investigated over the as-prepared 3D Pt/C composite. Typically, the oxidation of the small-molecule liquid fuels (EG, methanol, or ethanol) was evaluated in a standard three-electrode system using the same mole mass loaded on working glassy carbon electrodes (GCEs) in the media of 0.5 M KOH with 0.5 M liquid fuels.43 The mass loading of the electrocatalyst of the 3D Pt/C composite was kept fixed in each trial (20 μg). In the current work, commercial Pt black has been measured under the same conditions as reference for comparison at the same time. The cyclic voltammograms (CVs) were recorded at a scan rate of 50 mV s⁻¹ in 0.5 M H₂SO₄ solution according to the literature procedure,43 as demonstrated in Figure S18. The electrochemically active surface area (ECSA) for the 3D Pt/C composite was calculated to be 18.0 m² gPt⁻¹.44,45 Figure 3a–c reveals typical CV curves for small-molecule oxidations over both the 3D Pt/C composite and Pt black according to typical measurements in DAAFCs. There are two anodic peaks recognized as the features of the three reactions measured in the typical CV curves during positive and negative sweeps. There are anodic peaks revealed at approximately 0.06, 0.04, and 0.02V in the forward sweep, mainly resulted from the generation of Pt–OH and Pt–O species at electrode surface reacting with carbon-containing species like CO and HCOO⁻ from the oxidation of EG, CH₃OH, and C₂H₅OH. As noted, the catalytic performance of the electrocatalyst could be appraised by measuring the intensity of the forward anodic oxidation peak. As illustrated in Figure 3 and Table S1, it is clear that EGOR, MOR, and EOR mass activities over the 3D Pt/C composite are 565, 426, and 485 mA mgPt⁻¹, respectively, which are 2.8, 6.1, and 5.3 times higher than that of commercial Pt black (199, 70, and 92 mA mgPt⁻¹). As a result, the 3D Pt/C composite exhibited much higher activity compared to the representative catalyst of commercial Pt black. However, it is noted that in common, Pt and Pt-based catalysts are easily poisoned by the surface adsorption of some carbonaceous intermediates especially from the generation of CO due to alcohol oxidation. In the present investigation, it is expected that the tolerance of the composite would be improved with the presence of N-doping in the 3D Pt/C composite while we note that the tolerance to the carbonaceous species has not been enhanced in general due to the trace amount of N dopant. In general, the tolerance of an electrocatalyst can be evaluated using a vital parameter, I/I₀ which is the ratio of the forward anodic oxidation current density to the backward cathodic current density. In the present case, the I/I₀ value for EGOR, MOR, and EOR is calculated to be 1.50, 1.79, 1.32 and 2.03, 2.93, 1.06 over the catalyst of the 3D Pt/C composite and commercial Pt black, respectively, as seen in Table S2 and Figure 3a–c. In general, it is equivalent to Pt black even though it would be improved in the next step by applying dense doping of N component in addition to possible integration of a 3d metal that would be more effective for improving the tolerance of Pt-based catalysts.49–53

Durability is another critically important issue to assess a high-performance catalyst in electrochemical applications. In this work, a chronoamperometric (CA) detection was further carried out at −0.1 V for 4000 s. Compared with the measured result over the commercial Pt black, it is clearly found that the CA current density was well improved over the 3D Pt/C composite (Figure 4a,c,e). It exhibited that the current density over the catalyst of commercial Pt black decayed rather fast with respect to the 3D Pt/C composite. In addition, it is also found that the 3D Pt/C composite did not show obvious
Figure 4. Long-term durability measurements at −0.1 V over 3D Pt/C composite and commercial Pt black for EGOR (a), MOR (c), and EOR (e), respectively. In addition, the corresponding CV curves before and after the long-term durability measurements for EGOR (b), MOR (d), and EOR (f).

decrease in electrocatalytic activity after a 4000 s current−time test (Figure 4b,d,f, Table S3). However, the catalyst of commercial Pt black merely maintained 73.1, 48.8, and 29.3% of the primary mass activities for EGOR, MOR, and EOR, respectively (Figure S19, Table S3), performed under the same conditions. On the basis of above investigations, it implies that the 3D Pt/C composite with small Pt NPs supported by nitrogen-doped carbon is expected to fully exert synergy between the various components.

3. CONCLUSIONS

In conclusion, the efficient and facile strategy has been successfully developed and performed for the in situ preparation of the uniform porous spherical 3D Pt/C composite. Investigations reveal that the composite has been well controlled with numerous minute Pt NPs that are dispersed homogeneously in the monodisperse spherical carbon matrix without any obvious aggregation. Meanwhile, the as-prepared composite exhibits much better catalytic activity and stability for small-molecule oxidations electrocatalytically in alkaline solution as compared to the commercial catalyst of Pt black. The enhanced performance was resulted from the highly dispersive Pt NPs with very small size, porous structure, homogenous carbon distribution, the thin carbon shell, and trace N dopant in the spherical composite. This efficient in situ synthetic strategy would be available for the bulk fabrication of the electrocatalysts with simplified procedures, and it is expected that the present route would also be extended to some more highly active carbon-supported catalysts with multiple components besides the one as illustrated in the present work.

4. EXPERIMENTAL DETAILS

4.1. Materials. 4-Nitrophenol, potassium hydroxide, cyclohexane, chloroform, sulfuric acid, ethylene glycol, toluene, hexane, and ethanol were purchased from Sinopharm Chemical Reagent Ltd., China. Chloroplatinic acid (H₂PtCl₆) was purchased from Shanghai Chemical Reagent Co., China. The commercial Pt black catalyst was purchased from Alfa Aesar.

4.2. Synthesis of Materials. 4.2.1. Synthesis of Uniform Spherical Precursor. Typically, 94 μL of H₂PtCl₆ (0.077 mol L⁻¹) was added into a beaker with 5 mL of toluene. Under vigorous stirring, 0.3 g of 4-nitrophenol dissolved in 5 mL of deionized water was mixed with it. After that, the mixed solution was loaded into an autoclave and maintained at 150 °C for 10 h. After reaction, the sample was precipitated by ethanol and centrifuged. Then, the sample of uniform spheres was washed with ethanol and centrifuged repeatedly five times for the subsequent production of 3D Pt/C composite catalyst.

4.2.2. Synthesis of the 3D Pt/C Composite Catalyst. The as-prepared precursor of uniform spheres was annealed under a gentle gas flow of Ar (95%) + H₂ (5%) at 600 °C for 30 min.

4.3. Characterization. The structure, microstructure, and morphology of products were characterized by various analytic techniques. In detail, SEM spectra were recorded on JSM-6700F and TEM was carried out on a Hitachi H-7650. XRD was detected on a Philips X’Pert PRO X-ray diffractometer using graphite-monochromatized Cu Kα radiation (λ = 1.54182 Å). HAADF-STEM in addition to corresponding EELS and energy-dispersive X-ray spectrosopic mapping analyses were carried on a JEOL JEM-ARF200F TEM/STEM with a spherical aberration corrector. XPS spectra...
were acquired on an ESCALAB MK II using Mg Kr as the excitation source. Raman spectra were determined on a LABRAM-HR spectrometer with a 514.5 nm Ar+ laser. The weight percentage of carbon, hydrogen, nitrogen, and oxygen was characterized by elemental analysis, which was carried out on an EA, Elemental Vario EL cube over Thermal Conductivity Detector. TGA was performed on a SDTQ600 (TA Instruments) TG-DTA analyzer under the protection of nitrogen and air. The BET surface area and the Barrett–Joyner–Halenda porous distribution plots were measured on a Micromeritics ASAP 2020 accelerated surface area and porosimetry system. NMR spectra were measured on 400 MHz instruments with residue of CDCl$_3$ as the internal reference (7.26 ppm for $^1$H NMR).

4.4. Electrochemical Measurements. All of the electrochemical measurements were measured in a three-electrode system on an electrochemical work station (CHI660E, ChenHua, Shanghai, China). Pt sheet and Ag/AgCl (in saturated KCl solution) electrode were used as the counter electrode and the reference electrode, respectively, and all of the potentials were quoted with respect to the saturated Ag/AgCl electrode. For the measurement, a glassy carbon disk electrode (3.0 mm in diameter) was used as the working electrode. In the preparation of working electrode, the 3D Pt/C composite or reference catalyst was first transferred onto the glassy carbon disk electrode (~0.285 mg cm$^{-2}$) according to a standard treatment. ECSA were measured via integrating hydrogen adsorption charge on cyclic voltammetry (CV) carried out in a potential range from −0.2 to 1.0 V (vs Ag/AgCl electrode) in 0.5 M H$_2$SO$_4$ solution. After the electrode was activated (20 cycles) in H$_2$SO$_4$ solution, a CV data for the ECSA was acquired. Afterward, the electrode was transferred for the measurements of electrocatalytic alcohol oxidation. CVs for EGOR, MOR, and EOR were carried out in 0.5 M EG + C$_2$H$_5$OH + 0.5 M KOH, respectively, in the potential range from −0.1 to 0.4 V. All measurements were carried out with a scan rate of 50 mV s$^{-1}$ at room temperature.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02584.

Material including SEM image, XRD pattern of the sample after TGA measurement, XPS spectra, EELS line-scanning profile, N$_2$ adsorption–desorption isotherm and pore size distribution of the 3D Pt/C composite, SEM and TEM images, size distribution histogram, XPS spectra, $^1$H NMR spectrum of the spherical precursor obtained hydrothermally, mass activity of the 3D Pt/C composite and the commercial Pt black, and CV curves of the commercial Pt black before and after the long-term durability measurements (PDF)

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The authors declare no competing financial interest.

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