

RAPID COMMUNICATION

Biomimetic design of monolithic fuel cell electrodes with hierarchical structures



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Abstract

Despite the significant improvement of polymer electrolyte membrane fuel cell catalyst activities, a cost-effective and stable membrane electrode assembly is still lacking, which greatly inhibits the commercialization of this efficient and environmental friendly technology in stationary and transportation applications. The main reason is that the engineering of different components of an electrode, such as catalytically active metals, electron transport and reactant diffusion paths in a compatible way is very challenging. Here we show the design and preparation of a monolithic fuel cell electrode with a compatible wire on wire structure that mimics the configuration of a pine tree. We developed a procedure to make a flexible carbon thin film composed of porous nanofibers with a thickness of ~ 100 nm and centimeter scale lengths. Platinum nanowires (ca. 3 nm diameter) were deposited on these microscale carbon nanofiber films, resulting in a hierarchical structure. The platinum nanowires were then decorated with a porous bismuth coating to modulate the atomic structure and induce catalytic activity toward formic acid electrooxidation. The end result is a monolithic structure used as a fuel cell electrode that combines microscale diffusive pathways and nanoscale catalyst structures. Prepared by a process that is readily scalable, this design strategy offers a new way to tailor catalytic functions at a system level.

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Introduction

When powered by renewable fuels, polymer electrolyte membrane (PEM) fuel cells offer efficient and environmentally benign solutions for our future power source demands in sectors ranging from transportation to small electronic devices [1-3]. Despite two decades of intensive investigations and advancements achieved in fundamental electrochemistry and nanocatalyst synthesis, the implementation of PEM fuel cells at large scale is still hindered by the lack of cost-effective and operationally stable membrane electrode assemblies (MEAs) [4-10]. This situation is caused by the fact that most of fuel cell catalyst development efforts have focused on the specific aspect of fuel cell electrodes such as activity or durability, while less attention was paid on the engineering requirements of an MEA. This situation urges the investigation of component interfaces and their interaction within MEAs from a system point of view, while simultaneously considering the feasibility of mass-production [7,11-13].

Poor catalyst utilization and non-ideal mass transport properties commonly result from the traditional electrode fabrication strategy used for membrane electrode assembly (MEA) preparation. The strategy involves mixing of platinum nanoparticles (supported on carbon black or unsupported) in an alcohol solution with proton conducting ionomer, and then coating on a gas diffusion layer (GDL) using a brush or spray gun [14]. Introducing large size pores in the electrode was found beneficial for effective mass transport [15]; however, the optimization of Pt utilization in these traditional electrodes is very challenging. Several alternative strategies have been investigated to improve the mass transport properties, water management and catalyst utilization in fuel cell electrodes [16-26]. A straightforward strategy is the direct electro-deposition of electrocatalysts on carbon paper or graphene foam [16-18] that possesses an inherently open and interconnected porous structure. This structure leads to easy reactant transport and electron mobility, and has been demonstrated to provide direct formic acid fuel cell performance improvements in comparison to traditional MEA configurations [16,17]. A significant issue however is that the direct growth of highly dispersed catalysts on carbon fibers with microscale

diameters of $\sim 10\ \mu\text{m}$ (or $\sim 100\ \mu\text{m}$ for graphene foam) is very difficult. Furthermore, the true catalyst surface area that can be achieved on carbon papers or graphene foams is limited by the small surface area of these substrates. Although employing self-assembled carbon nanotube meshes offers higher substrate surface areas [19,20], the uniform and stable integration of Pt nanocatalysts on these supporting materials remains challenging. The nanostructured thin film catalysts developed by physical vapor deposition of Pt or Pt alloy onto organic whiskers represent the state of the art $\text{H}_2\text{-O}_2$ fuel cell catalysts from the aspect of low catalyst loading performance and durability [21]. However, the uniformity of deposited catalytic metals through the whole thickness of the organic whisker substrate is still far from ideal. Furthermore, the use of these catalysts in liquid fuel cells, such as direct methanol or formic acid fuel cells is very challenging because the production of thicker catalyst layers using the physical vapor deposition method is not possible. On the other hand, nanoporous metals have been investigated as catalyst supports in both $\text{H}_2\text{-O}_2$ and liquid fuel cells [22-25]. With ultra-high Pt utilization and fast electron transportation within the inter-connected metal ligaments, these catalysts show the highest Pt mass specific performance in real fuel cells [25]. However, the mass transport within these 20-30 nm pores, especially for liquid fuel cells, effectively limit the areal power densities of these nanoporous metal based electrodes [25]. Ordered macroporous Pt electrodes with pore sizes of $\sim 500\ \text{nm}$ can overcome this by readily facilitating mass transfer, although the optimization of Pt utilization in this structure is very challenging and the electrode preparation process is very complex, which may limit its real application [26]. In order to achieve high performance in fuel cell with optimized Pt catalyst utilization, the design of catalytic electrode should be started from a system point of view and the compatibility of preparation process with existing technology should also be considered [7,11].

In nature, many processes rely on complex structures that are compatibly organized with different levels of sub-structures, leading to functional, hierarchical design. A characteristic example is a pine tree, where the needle-like leaves are grown uniformly on the surface of twigs, which in turn are attached to the branches (see Figure 1a

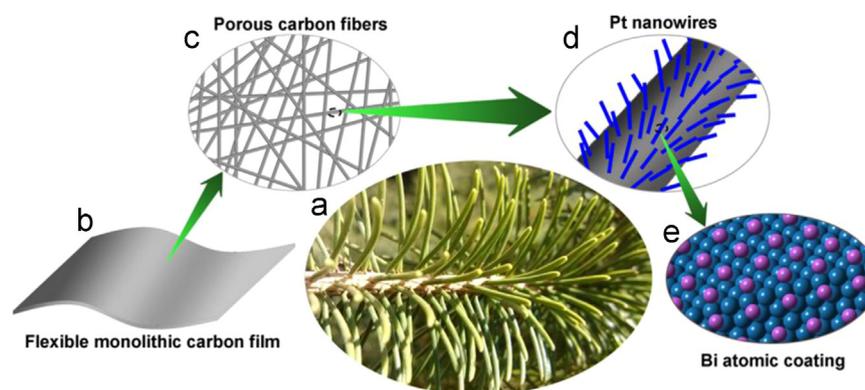


Figure 1 Hierarchical structures in nature and by design. (a) Optical photo of a branch showing the hierarchy wire on wire structure of a pine tree. (b-e) Monolithic thin film catalyst composed of porous carbon nanofibers on top of which Bi decorated Pt nanowires were grown.

for a close up optical photo). This structure spans from millimeters to meters in dimension, and allows for the efficient mass transport from the branches to leaves of a pine tree. Here, by mimicking a pine tree, a monolithic fuel cell electrode with a hierarchical wire on wire structure is designed (see Figure 1). First, a flexible thin film composed of net-like carbon nanofibers was prepared by annealing of an electrospun polyvinylpyrrolidone titanium dioxide composite (PVP-TiO₂) nanofiber mat (Figure 1b). The carbon net (denoted as CN) film has a structure conducive to fast mass transport within the micrometer size pores, and offers a high degree of interconnectivity of the centimeter length nanofibers to ensure electron conductivity across the entire film (Figure 1c). Second, Pt nanowires with diameters of 2–5 nm and lengths of ~100 nm were grown uniformly on the surface of the CN film (Figure 1d). These thin Pt nanowires guarantee high Pt utilization and the simple preparation method allows easy tuning of the Pt loading and nanowire lengths, making the process amenable to application specific designs. Third, the surface of Pt nanowires was decorated with an ultra-thin porous Bi coating layer to show the feasibility of changing the surface state of these electrodes to be application specific (Figure 1e).

Materials and methods

Carbon net preparation

All the chemicals are purchased from Sigma Aldrich. To make electrospinning solution, 0.135 g polyvinylpyrrolidone (PVP, molecular weight: 1.3 million) was dissolved in 2.5 ml ethanol and 0.5 ml titanium butoxide was dissolved in 1 ml ethanol+1 ml acetic acid, respectively. The above two solutions were mixed together by hand-shaking and degassed by brief ultrasonication before loading in 10 ml syringe. Electrospinning was conducted under nitrogen protection. The humidity was controlled between 25% and 35%. The electrospinning solution was sent to a syringe needle at a speed of 1 ml/h using a syringe pump. The distance between the syringe needle tip and collecting Al foil was controlled to be 10 cm. The voltage applied was controlled to be 20 kV by the power source. To make a free standing electrospun film, a gas diffusion layer (GDL) was used as collecting electrode, which was attached in the middle of the Al foil. The thickness of electrospun film could be easily controlled by changing the duration of electrospinning. The electrospun film was stored in ambient conditions overnight to allow the completion of titanium butoxide hydrolysis. The free standing electrospun film was obtained by carefully detaching PVP-TiO₂ composite film from the GDL.

The free standing electrospun film was sandwiched by two pieces of GDL and annealed in the protection of Ar (70 ml/min) using a programmed heating procedure. After purging the furnace tube for 30 min using Ar, the temperature was allowed to rise from 20 °C to 500 °C in 9 h. Then the temperature was held for 2 h at 500 °C before cooling down to room temperature. A monolithic flexible carbon net composed of porous carbon nanofibers was obtained.

Growth of platinum nanowires on carbon net

PtNW growth solution was made by mixing 6 ml 20 mM H₂PtCl₆, 2 ml formic acid and 34 ml ultra-pure water. PtNWs growth was conducted at room temperature for 3 days by adding the solution into a Petri dish containing pre-treated carbon net. After cleaning with ultra-pure water, the carbon net supported platinum nanowire catalyst (CN-PtNW) was dried in oven at 60 °C overnight.

Bismuth deposition

To make the bismuth deposition solution, 5 mM Bi₂O₃ was added into 0.1 M HClO₄ to make a clear mixed solution. CN-PtNW was attached to gold foil and inserted in the mixed solution as a working electrode. Bismuth deposition was conducted by applying -0.1 V potential for 400 s using a saturated calomel electrode (SCE) as the reference electrode. After Bi deposition, the CN-PtNW-Bi electrode was cleaned with ultra-pure water and dried in an oven at 60 °C overnight.

Preparation of gas-diffusion-layer supported Pt black electrode (GDL-PtB)

The catalyst slurry was made by adding the proper amount of ethanol and Nafion (15%) in ultra-pure water wetted platinum black (PtB, Sigma Aldrich). The dry weight ratio between Nafion and PtB was controlled to be 1:3. The slurry was sprayed onto gas diffusion layer (GDL, SGL 10 BB) using a spray gun while the GDL was heated at 60 °C for fast drying. The catalyst loading was controlled to be 3.6 mg/cm² by micro-balance weighting. The GDL supported Pt black electrode (GDL-PtB) was cut into proper shape for electrochemical testing.

Electrochemical testing

The electrochemical and electrocatalytic properties of CN-PtNW, CN-PtNW-Bi and GDL-PtB catalysts were evaluated in 0.1 M HClO₄ and 0.1 M HClO₄+0.05 M HCOOH solutions. A SCE was used as reference electrode and the electrode potentials were converted to the RHE scale. The catalyst films were attached onto a gold foil and activated using cyclic voltammetry (CV) between 0 and 1.3 V in Ar purged 0.1 M HClO₄ solution for around 10 cycles at a scan rate of 10 mV/s. Then the catalytic activities were evaluated by CV in 0.1 M HClO₄+0.05 M HCOOH solution at a scan rate of 1 mV/s.

Physical characterization

Scanning electron microscopy (SEM) characterizations were performed on a Zeiss ULTRA plus field emission SEM with a working distance of 10 cm. All the samples were attached to conductive carbon tape directly for imaging. PVP-TiO₂ samples were gold sputtered to increase the sample conductivity. All the samples were dispersed in ethanol by brief ultrasonication and loaded onto a copper grid for transmission electron microscopy (TEM) characterizations using a

JEOL 2010F TEM and FEI Titan 80-300 HB working at 200 kV. Energy dispersion X-ray spectroscopy (EDS) was performed on the Titan device. Thermogravimetric analysis (TGA) was conducted in air using a Q500 V20.13 TA instrument with a heating rate of $2\text{ }^{\circ}\text{C min}^{-1}$. X-ray diffraction (XRD) experiments were performed on an Inel XRG 3000 diffractometer using monochromatic Cu K α X-rays (wavelength: 0.154 nm). X-ray photoelectron spectroscopy (XPS) was performed on a PHI Quantera device.

Results and discussions

Carbon net preparation

To make a suitable substrate that effectively bridges the gap between the macro- and nano-world, a carbon fiber mat composed of ~ 100 nm diameter nanofibers was prepared (Figure 2). The mat, consisting of randomly orientated nanofibers, was made by electrospinning a solution containing titanium butoxide and polyvinylpyrrolidone (PVP, see *Methods* for details) [27]. Electrospinning has been reported to be able to make randomly or controlled orientated nanofibers with length of several inches at low processing cost and flexibility of scale up [28,29]. Although the making of a nanofiber mat with ultra-thin thickness has been reported with a ring collecting electrode [29], the making of free standing thin film on a more easily handling substrate such as Al foil is challenging because the polymer film tends to stick on the substrate tightly. Here we found that by using a gas diffusion layer (GDL) as a collecting substrate in front of the grounded Al foil electrode, the polymer film could be easily peeled off from the GDL and a free standing electrospun film with thicknesses down to a few micrometers could be obtained (Figure 2a and b). As expected, the thickness of the polymer nanofiber film increases with electrospinning time, offering a straight forward way to control the thickness of the final carbon film (Figure S1). After electrospinning, the film was left under ambient conditions overnight to allow full hydrolysis of the titanium butoxide. The resulting PVP-TiO₂ film could be easily peeled off with almost no left over on GDL, with the example shown in Figure 2b corresponding to a $\sim 10\text{ }\mu\text{m}$ thick prepared by electrospinning for 3 min. The film is very flexible because of the ultra-thin thickness and mechanically robust. With shorter electrospinning time, films thinner than $10\text{ }\mu\text{m}$ could also be obtained. Four different types of GDL substrates were investigated, all of which gave similar flexible thin films despite their significant microstructural differences (Figures S2-4). The weaker adhesion of the electrospinning film on GDL substrates in comparison to the Al foil should be ascribed to the rough surface and unique hydrophobic properties of the GDL.

The electrospun PVP-TiO₂ film was sandwiched between two pieces of GDL and subjected to a heat treatment at $500\text{ }^{\circ}\text{C}$ under the protection of flowing Ar as shown in Figure 2c. After annealing, the white PVP-TiO₂ film turns into a black film with flexibility and mechanical integrity. The film could fully recover from high curvature by bending (Figure 2d and e). In contrast, the film annealed

under air conditions results in a very brittle white film composed of TiO₂ nanofibers (Figure S5). Scanning electron microscopy (SEM) imaging (Figure 2f) shows that the film is composed of nanofibers with a thickness of around 100 nm and the length of which is too long to be measured with SEM. Compared with the nanofibers in PVP-TiO₂ film, the carbon nanofibers are much thinner which explains the $\sim 25\%$ lateral shrinkage of the film during annealing. Interestingly, transmission electron microscopy (TEM) images show that the nanofibers are porous, which is distinct from the expectation that carbon-TiO₂ composite structure without pores should be formed. The fact that a carbon-TiO₂ composite structure without observable pores was obtained if the PVP-TiO₂ film was not sandwiched by GDL or sandwiched between GDLs previously used during annealing (Figure S6) indicate an in-situ removing of TiO₂ happened during annealing with the presence of GDL. Nanoparticle template method has been used to make an electrospinning fiber with porous structures, however this is the first time a porous carbon fiber film is made with one step annealing process. As the GDL is coated with polytetrafluoroethylene (PTFE) to change its hydrophilicity, we propose that PTFE decompose at high temperature and release a corrosion inducing gas which reacts with TiO₂, leading to its removal and the porous interior structure in the carbonized nanofibers.

Thermal gravity analysis (TGA) results shown in Figure S7 reveal an onset of weight loss for both GDL and pure PTFE at approximately $470\text{ }^{\circ}\text{C}$. This indicates that the PTFE content of the GDL begins decomposition below the $500\text{ }^{\circ}\text{C}$ temperature used to anneal the nanofibers and induce porosity. Elemental line scan on a porous carbon nanofiber and X-ray photoelectron spectroscopy (XPS) results (Figure S8 and S9) show the presence of fluorine and almost total removal of Ti (also demonstrated with X-ray diffraction, XRD results shown in Figure S10) all of which indicate the removal of TiO₂ by reacting with corrosive fluorine containing compounds. This is consistent with the fact that TiF₄ could sublimate at high temperature [30]. The fact that most of the mass lost of PVP-TiO₂ during the annealing happens before $\sim 400\text{ }^{\circ}\text{C}$ (Figure S7) indicates the removal of TiO₂ happens after the starting of PVP carbonization [31] which rationalizes the formation of the porous structure of the carbon nanofibers. To the best of our knowledge, this is the first demonstration of a flexible, highly porous carbon nanofiber net prepared by a one-step annealing process, which greatly simplifies the procedure for future commercial implementation.

The conductivities of CN film and carbon-TiO₂ film were measured to be 0.057 and 0.14 S/cm , respectively. Lower conductivity of CN films in comparison with carbon-TiO₂ films may be caused by different structural or surface properties induced during the corrosive removing of TiO₂. High resolution TEM (HRTEM) imaging shown in Figure S11 demonstrates an amorphous carbon structure with some graphitization. It is expected that the conductivity of the film could be further improved by increasing the annealing temperature and by extension, the degree of graphitization. This could have important implications for applications such as super-capacitors and battery electrodes, but it is not critical for the design of our fuel cell catalyst as will be discussed below [32].

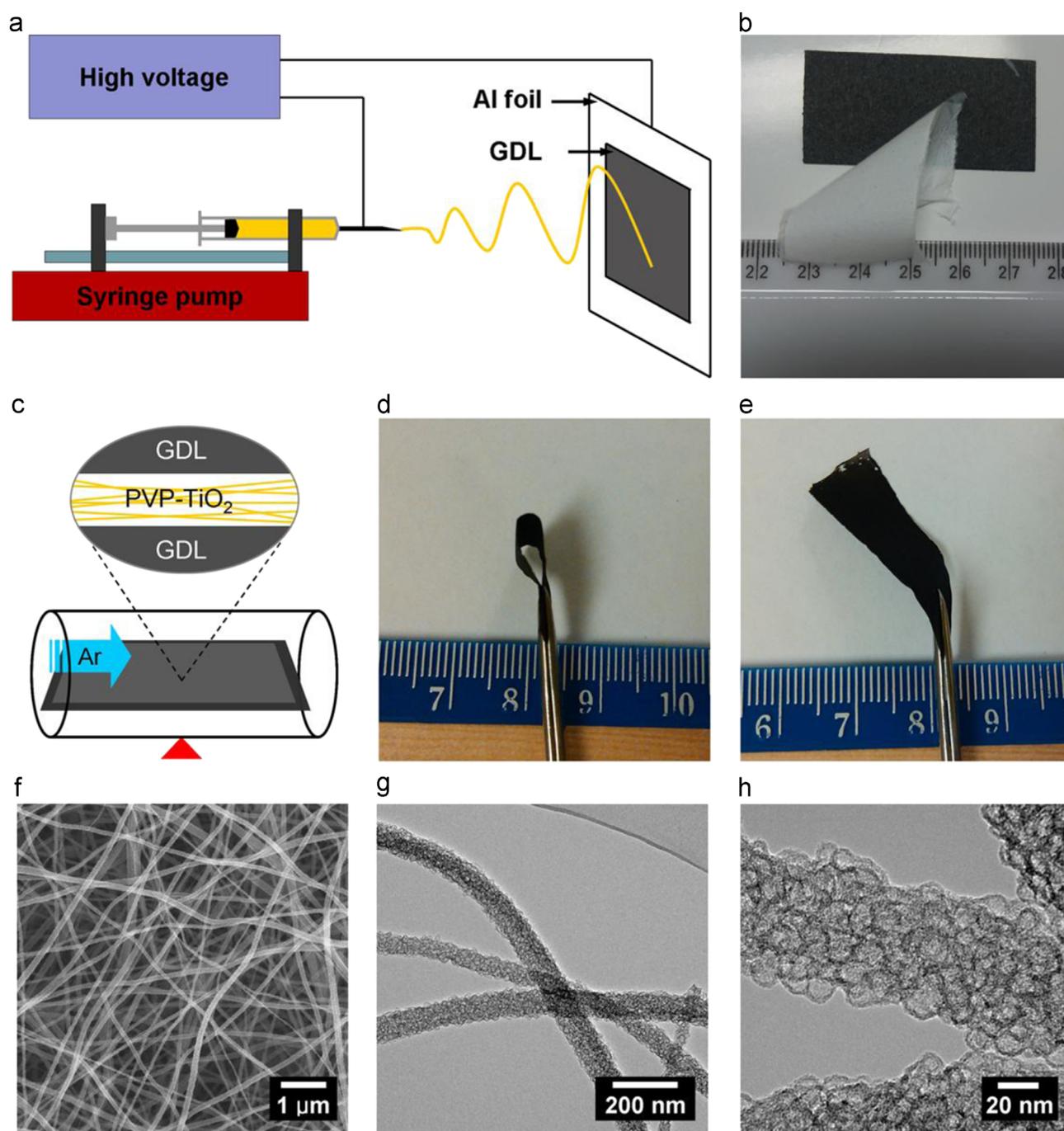


Figure 2 Carbon net composed of porous carbon nanofibers. (a) Schematic illustration of the making of PVP-TiO₂ thin film by electrospinning. (b) Optical photo of PVP-TiO₂ thin film. (c) Schematic illustration of the making of carbon net using a simple annealing method. (d) Cross-section view optical photo of carbon net during bending. (e) Cross-section view optical photo of carbon net after bending and releasing. (f) Plane-view SEM image of carbon net. Low (g) and high (h) magnification TEM images of porous carbon nanofibers.

Growth of platinum nanowires on carbon net

Platinum nanowires were deposited on the CN film using a wet chemical method, where H₂PtCl₆ is reduced by formic acid at room temperature. This facile and green method has been demonstrated to be able to grow on Pt nanowires with controlled length on different substrates with almost 100% yield [33-36]. Interestingly, we found the CN film prepared

here is an ideally suitable substrate for this technique. As shown in Figure 3a and Figure S12, the micro-size porous structures of the monolithic CN film allows the free diffusion of platinum and reducing agent reactants through the whole film. Conversely, when using high surface area carbon supports, they will settle down to the bottom of the reaction vessel and their high packing density will hinder the penetration of the deposition solution into the

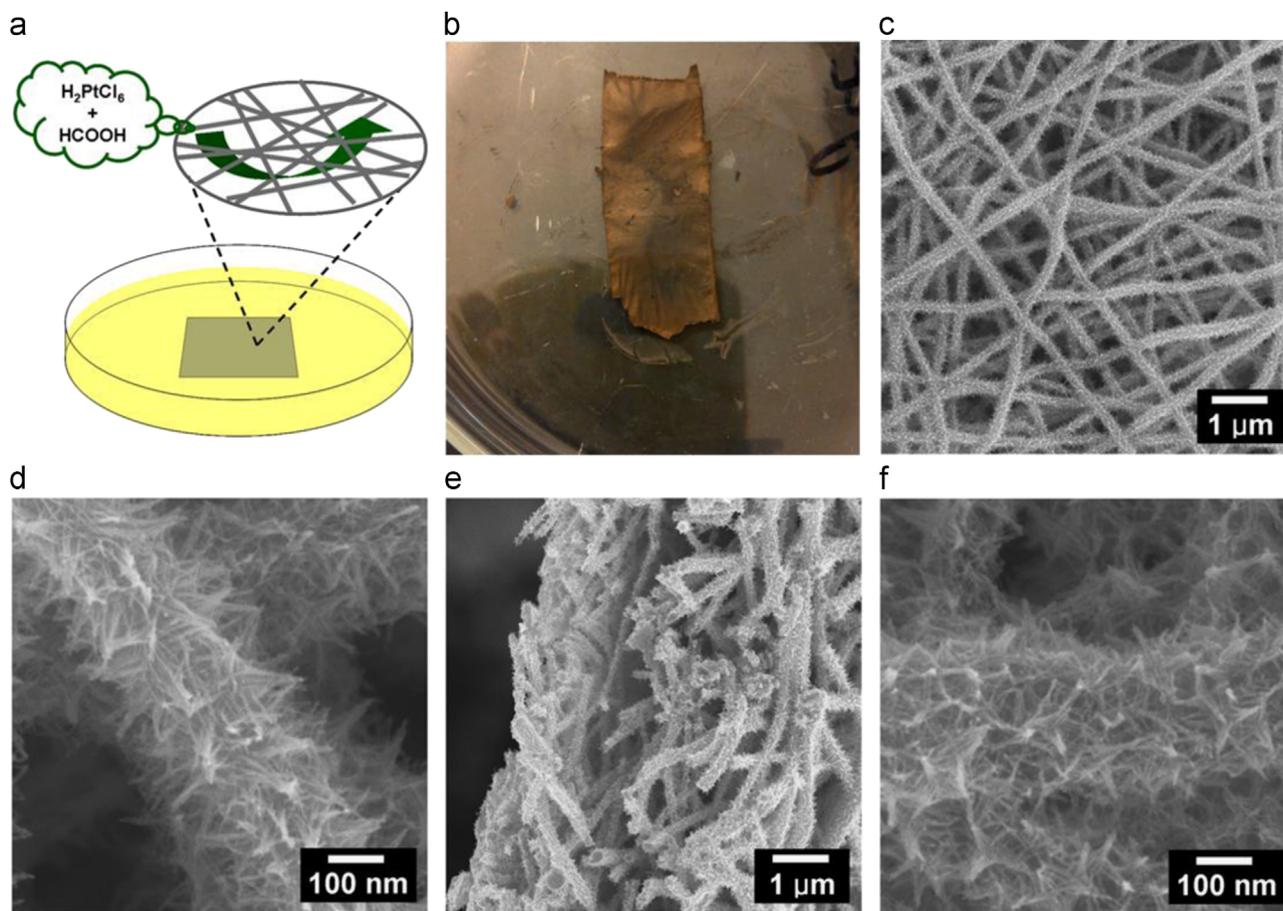


Figure 3 Platinum nanowires on carbon net. (a) Schematic illustration of the growing of platinum nanowires on carbon net. Plane-view optical photo (b), plane-view low (c) and high (d) magnification SEM images, cross-section SEM image (e), and backside plane-view high magnification SEM image (f) of platinum nanowires on carbon net.

underlayers. In fact, we do observe a more uniform growth of Pt nanowires on carbon black when using identical solution volumes in a Petri dish compared to a smaller bottom vial. Even in a petri dish, it is only possible to achieve good Pt nanowire dispersion when the carbon black concentration in the solution is sufficiently low to allow the formation of an ultra-thin packing layer at the bottom of the reaction vessel. When the concentration of carbon black is too high, uniform growth of Pt nanowires could not be achieved.

After growth of the Pt nanowires on the CN film, the apparent dimensions of the thin film did not change. Flexibility and mechanical robustness were also retained, although a color change from black to brown was observed (Figure 3b). The low resolution SEM image (Figure 3c) shows an increase of the diameter and a uniformly coated nanofiber surface. High resolution and cross-sectional SEM images (Figure 3d-f, Figure S13) show a uniform layer of nanowires grown on the surface of carbon nanofibers throughout the entire thickness of the CN film. As mentioned previously, this three dimensional uniformity for microscale components is very difficult to achieve by conventional techniques. XRD (Figure S10) and elemental line scanning (Figure S14) confirmed that the nanowires are face centered cubic (fcc) Pt. The uniform nucleation of Pt nanowires on the surface of carbon

nanofibers is likely associated with the dopant-rich (N, O, and F) surface of the nanofibers. The presence of these dopants is demonstrated by XPS (Figure S9), and this notion is consistent with previous reports on the importance of surface functional species for facilitating Pt nucleation and growth [36,37]. In our previous work, we demonstrated the beneficial impact of sulfur dopant species in graphene for greatly enhancing the nucleation density of platinum nanowires [36]. The uniform length and density of Pt nanowires grown on the whole surface of CN film demonstrates the free mass transfer through the thin film. This guarantees the fast diffusion of fuels to the catalytic surface of Pt nanowires in real operation condition. The generated electrons will transport to external circuit through the inter-connected carbon nanofiber networks. It is worth mentioning that the conductivity of Pt nanowire on carbon net (C-PtNWs) film is measured to be 22.7 S/cm, which is ~400 times higher than the pristine carbon net film. This means that the conductivity channel within C-PtNWs film is totally different from that of CN film. A close look at the structure of C-PtNWs with TEM and HRTEM reveals that these single crystal Pt nanowires with diameter of 2-5 nm and length of ~100 nm are grown on the surface of carbon nanofiber tightly (the Pt nanowires on carbon nanofiber structure are intact even after sonication). Importantly, they have a

high degree of structural overlap and interconnectivity which offers new electron transport channels in addition to the carbon nanofibers themselves.

Surface decoration

Until now, we demonstrated the successful preparation of a monolithic electrode with compatibly organized wire on wire hierarchical structure that mimics the functional architectures of many living species, such as the branch and needle structure of pine trees. Previous work demonstrated the length of Pt nanowires could be easily controlled with this method [34]. Shorter Pt nanowires could be made by increasing the ratio between the CN film and reaction solution for H₂/O₂ fuel cells application because usually high performance could be obtained with low Pt loadings. When powered by liquid fuels such as formic acid or ethanol, Pt catalysts are prone to be poisoned by reaction intermediates, which make the decoration of the Pt surface with other atoms necessary. Tin oxide has been shown to greatly improve the catalytic activity of Pt surface toward ethanol electro-oxidation by offering hydroxide to facilitate the removing of poisoning reaction intermediates [38,39]. Decorating of Pt surface with other metals such as Au [23], Bi [25,40,41], Pd [42], Pb [43], Sb [44,45] etc. will greatly enhance the catalytic performance of Pt surface toward formic acid electro-oxidation reaction by offering hydroxide or confining specific atomic ensembles. Here, using Bi deposition as a demonstrator, we show the feasibility of tuning the surface properties of Pt nanowires for specific applications. As the C-PtNWs films are monolithic electrodes with every surface Pt atom accessible to both electrons from external circuits and ions in solution, it is easy to modify the electrode with a uniform Bi coating using a direct electro-deposition process. After Bi deposition, no morphology changes could be observed from SEM images shown in Figure S15. The TEM images of electrode after Bi deposition were shown in Figure 4d-f. Low magnification TEM also shows no difference with sample before Bi deposition, demonstrating a very uniform coating of Bi absent of any aggregation and particle formation. A close look at the surface reveals a porous ultra-thin layer of Bi coating (1-3 atomic layers) uniformly covered the surface of Pt nanowires (see Figure 4e and f). The Bi-Pt atomic ratio was determined to be 6:94 with energy dispersive X-ray spectroscopy (EDS). This is consistent with the ultra-thin Bi layer result from TEM. The uniform distribution of Bi is further conformed by the EDS line scan shown in Figure S16.

Electrochemistry and electrocatalytic activities

The electrochemical properties of C-PtNW and C-PtNW-Bi electrodes were tested in 0.1 M HClO₄ with Pt black catalysts coated on GDL (GDL-PtB) as a comparison. From the cyclic voltammetry curves shown in Figure 5a, one can see the characteristic feature of Pt electrodes, including the hydrogen under potential deposition/desorption (H-UPD) peaks between 0 and 0.4 V and Pt oxidation/reduction peaks at higher potentials. The C-

PtNW sample not only shows larger mass specific currents but also less Pt redox and hydrogen under-potential adsorption/desorption peak hysteresis compared with the GDL-PtB electrode, indicating a higher specific surface area with much easier reactants accessibility. The good conductivity caused by the overlapping of Pt nanowires offers the electrode with fast electron transport which together contributes to the less hysteresis in CV curves. The specific surface area of C-PtNW sample is double of Pt black on GDL electrode (33.5 vs. 16.7 m² g_{Pt}⁻¹). These results demonstrate the advantage of designing a hierarchical electrode structure with micrometer size pores for easy reactant transport and nanometer size Pt catalysts for high noble metal utilization. Compared with C-PtNW, the C-PtNW-Bi sample shows increased oxidation/reduction peaks at higher potentials and decreased H-UPD peaks indicating the successful deposition of Bi. The presence of the H-UPD peaks indicates the accessible of the Pt surface by solution is not compromised, which is consistent with the porous structure of the Bi coating shown in the TEM images. Without Bi decoration, Pt surfaces are easily poisoned at lower potentials typically below 0.65 V vs. RHE (Figure 5b). However, the C-PtNW sample shows much improved catalytic activity toward formic acid electro-oxidation at higher potential compared with the GDL-PtB electrode. For example, at 0.72 V vs. RHE, C-PtNW shows activity of 7.85 mA mg_{Pt}⁻¹, while GDL-PtB has already reached the diffusion limiting current of ~2.7 mA mg_{Pt}⁻¹, indicating a sluggish mass transportation in GDL-PtB electrode. The 2.9 fold higher activity is a solid evidence to support the structural superior of C-PtNW. To make a catalyst layer for MEA, traditional method such as GDL-PtB sample uses Nafion as a binder and proton conductor. This will introduce significant mass transfer resistance. While our sample is a free standing membrane, no ionomer is needed to make the MEA. This, together with the micro-sized pore structure, provides much less mass transfer resistance in the C-PtNW film. As expected, the C-PtNW-Bi sample shows much improved catalytic activity toward formic acid electro-oxidation reaction. The Pt surface area and mass specific activities of C-PtNW-Bi catalyst are 33 (0.12 vs. 0.0036 mA cm_{Pt}⁻²) and 16 (9.3 vs. 0.6 mA mg_{Pt}⁻¹) times higher than the GDL-PtB sample, respectively. It is believed that the decoration of Bi on the surface of Pt will inhibit the formation and also facilitate the removal of poisoning intermediates such as CO [41]. The 50 times Pt ECSA specific activity enhancement (0.12 for C-PtNW-Bi vs. 0.0024 mA cm_{Pt}⁻² for C-PtNW) reported here is much higher than the 24 times enhancement reported in the literature [25]. It is well known that the catalytic activities of ad-atom decorated Pt surfaces toward formic acid electro-oxidation are highly coverage dependence and catalytic activities as high as 200-fold enhancement compared with pure Pt surface could be achieved with higher Bi coverage [41]. However, the mass specific activity may be sacrificed with the highest Bi coverage. It is expected that a systematic investigation of the catalytic activities with function of Bi coverage will result in even higher catalytic activities at suitable coverage and this phenomena is being explored further.

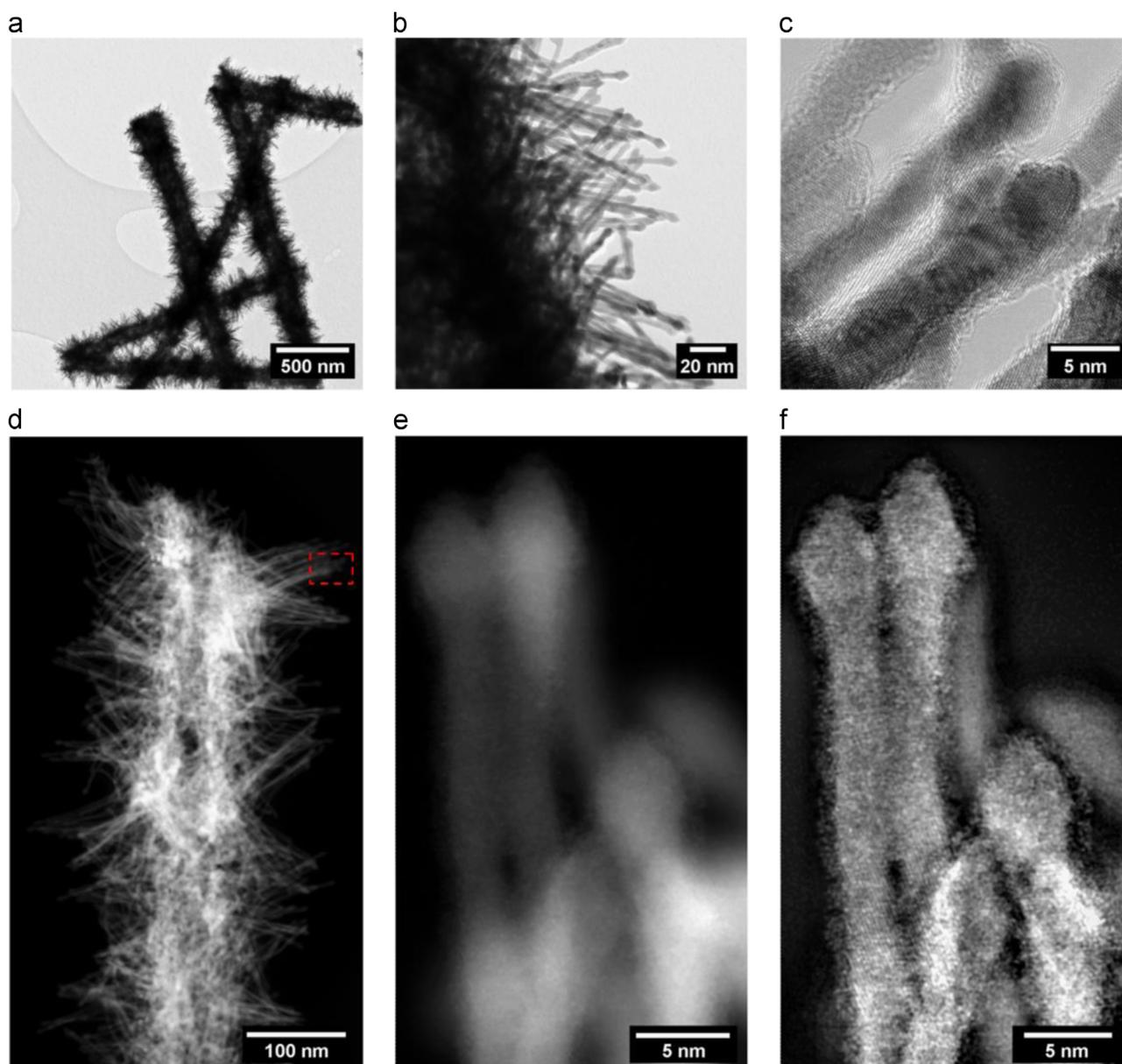


Figure 4 TEM images of platinum nanowires on carbon net with or without Bi decoration. Low (a) and high (b) magnification, and high resolution (c) TEM images of platinum nanowires on carbon nanofibers. Low magnification (d), high resolution (e), and fast Fourier transform filtered and (f) TEM images of Bi decorated platinum nanowires on carbon nanofibers.

4. Conclusions

In conclusion, a flexible carbon film composed of ultra-long porous carbon nanofibers was made using a one-step annealing procedure. On the basis of this net like carbon mat structure, by mimicking a pine tree, a monolithic fuel cell electrode with compatible descending hierarchical structure was made by growing Pt nanowires on the surface of porous carbon nanofibers using a solution method. This electrode with demonstrated high surface area, good mass diffusion and electron transportation properties and catalytic adjustability for specific applications is ready to be incorporated into membrane electrode assembly and feasible for mass production. The principle of the first system material engineering procedure in fuel cell electrode design is expected to

be borrowed in designing similar energy conversion and storage systems such as super-capacitor and batteries.

Author contributions

R.W. and Z.C. conceived and designed the experiments; R. W. synthesized the catalysts and tested the performances; R. W. and D. L. performed SEM characterizations; R. W., D. H. and S. P. performed TEM experiments; F. H., V. C., G. L., G. J., and J. C. helped with experiments; G. B. and Z. C. supervised the project; R. W., D. H. and Z. C. co-wrote the paper. Everyone discussed and reviewed the manuscript.

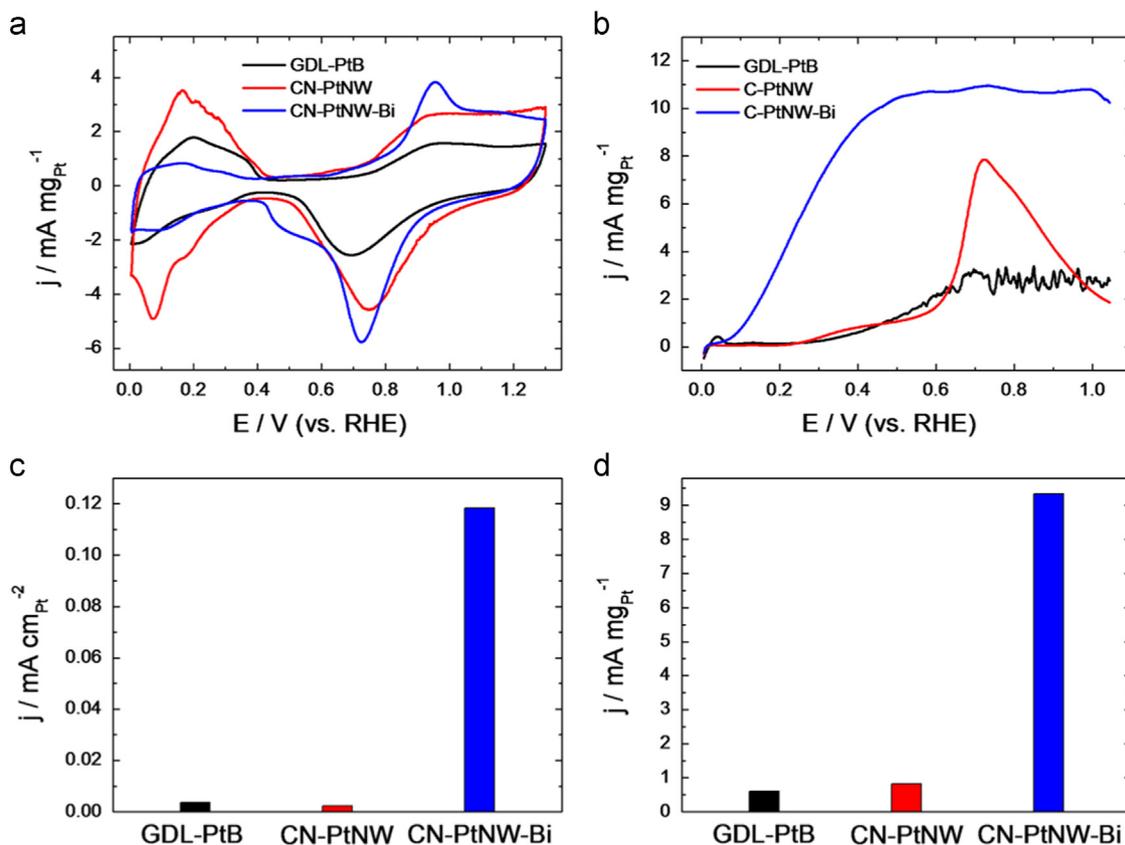


Figure 5 Electrochemical and electrocatalytic properties of platinum black on gas diffusion layer, platinum nanowires on carbon net, and Bi decorated platinum nanowires on carbon net catalysts. Cyclic voltammograms in 0.1 M HClO₄ (a, scan rate: 10 mV/s) and 0.1 M HClO₄+0.05 M HCOOH (b, scan rate: 1 mV/s). Platinum electrochemical surface area specific and (c) mass specific (d) catalytic activities in 0.1 M HClO₄+0.05 M HCOOH at 0.4 V; scan rate: 1 mV/s.

Competing financial interests

The authors declare no competing financial interests.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2015.11.033>.

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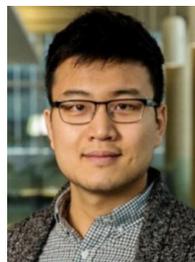
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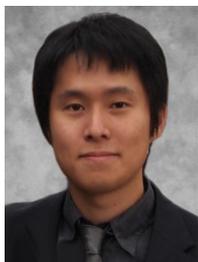
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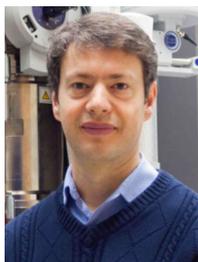
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