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Ultra-low mass loading of platinum nanoparticles on bacterial cellulose derived carbon nanofibers for efficient hydrogen evolution

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ABSTRACT

The ultra-low loading amount of Pt nanoparticles on three-dimensional bacterial cellulose derived carbon nanofibers (BCF) was achieved by using a modified atomic layer deposition (ALD) process for hydrogen evolution reaction (HER). The only 5 cycles of ALD led to a high dispersion of Pt nanoparticles on BCF surfaces with an average size of 2 nm, possessing an as low as 0.87 wt% of mass loading. The HER catalytic performance revealed that the as-prepared Pt/BCF have good catalytic activity and stability. The present work provides a general strategy for minimizing the demand of precious-metal catalysts while maintaining their high catalytic efficiency.

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1. Introduction

Because of the deteriorating environment and depleting of fossil fuels, as a high-energy-density carrier of clean energy, hydrogen has attracted tremendous attention recently [1–3]. The direct generation of hydrogen from the environmental-friendly electrolysis of water is one attractive strategy [4–9]. While the hydrogen evolution reaction (HER) of direct electrochemical splitting of water requires an efficient and robust catalyst to reduce the reaction overpotential and to increase the catalytic current density [1,9]. Currently, among various catalyst materials, noble metals, especially platinum (Pt) has been regarded as the best electrocatalyst that provides the highest electrochemical activity toward the HER [10–15]. However, the high cost of Pt limits the according economic viability and hinders the widespread utilization. Though alternative electrocatalysts based on earth-abundant elements such as transition metal chalcogenides (TMCs) have been explored to reduce the costs [7,9], the electrochemical catalytic performances of these developed materials are still lag behind Pt in terms of the HER. Thus, feasible option approaches, which could reduce the loading amount of Pt while retaining the electrocatalytic activity for HER, become very urgent.

Besides Pt utilization, the use of large-surface-area conductive supports for a given catalyst is another way to increase the catalytic activity of HER, such as carbon nanotubes, graphene and carbon nanofibers [16]. In particular, three-dimensional (3D) carbon nanofiber aerogel that derived from biologic bacterial cellulose (BC) has been explored for HER, owing to the environmental friendliness, cost effectiveness, light-weight, high inertness in harsh electrochemical conditions, large surface area as well as good conductivity for intermediation transport [17,18]. However, it is still challenging to achieve low-loading and high dispersion of Pt nanoparticles on the surface of BCF by the traditional chemical deposition, electrodeposition or physical vapor deposition processes. Therefore, a strategy based on low-loading amount of Pt nanoparticles highly-dispersed on high-surface-area of supports to minimize the overall raw material cost is imperative.

Recently, as a modified chemical vapor deposition technique, Atomic layer deposition (ALD) allows conformal and homogenous coating on large-surface 3D structures with precise controllable thickness at atomic level [19–21]. For the Pt ALD process, the certain chemical reaction results in the nucleation of isolated islands on the support surface. The islands grow with increasing ALD cycles and finally coalesce into a film [22–24]. The growth process of the isolated islands has been used for direct depositing Pt particles with diameters less than 10 nm [23]. Combining with our modified ALD process [24], the conformal Pt isolated-islands could highly

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disperse Pt nanoparticles on large surfaces of conductive supports, while decreasing the utilization of Pt for HER application.

Herein, to minimize the loading amount of Pt while maintaining their catalytic performance, we grafted ultra-low loading amount of Pt (0.87%) nanoparticles with diameters ranging from 1 to 3 nm on surfaces of 3D carbon nanofibers, via only 5 cycles of ALD process. With the intervening of low nitrogen filling steps, the Pt nanoparticles were highly dispersed on nanofiber surfaces with a high surface-to-bulk atomic ratio. Electrochemical measurements showed that the as-prepared ultra-low mass loading Pt nanoparticles on BCF catalyst has as good electrocatalytic activity as commercial Pt/C catalyst for HER. The present investigations demonstrate that the combination of low-nitrogen-filling ALD process and large-surface BCF is a powerful strategy that could efficiently minimize the Pt demands for efficient hydrogen evolution.

2. Experimental

2.1. Preparation of BCF aerogels

Purified BC pellicle with fiber content of ~1% (vol/vol) was provided by Yu Lab (University of Science and Technology of China) [17,18]. The wet BC pellicles were first cut into rectangular shape with sharp blade, frozen in liquid nitrogen and then freeze-dried in a bulk tray dryer (Labconco Corporation, Kansas City, MO, USA) at a sublimating temperature of -50°C and a pressure of 0.04 mbar. The dried BC aerogel was then pyrolyzed under flowing N_2 at 800°C to generate black BCF aerogel.

2.2. Preparation of Pt/BCF electrode

Grafted of Pt nanoparticles on BCF was performed on Picosun Sunale R150 ALD reactor by low-nitrogen-filling ALD process as we previously reported [24]. The precursors used for Pt growth were trimethyl(methyl cyclopentadienyl)platinum(IV) ($\text{Pt}(\text{MeCp})\text{Me}_3$) (Sigma Aldrich) and O_2 . The temperature of Pt precursor was held at 80°C . The substrate temperature for Pt growth was 220°C . And the typical ALD cycle consisted of $\text{Pt}(\text{MeCp})\text{Me}_3$ pulsing (1.0 s)–low N_2 filling (60 s)– N_2 purging (30 s)– O_2 pulsing (1.0 s)–low N_2 filling (30 s)– N_2 purging (30 s).

2.3. Characterization

Transmission electron microscopy was performed by JEM-ARM 200F operating at an accelerating voltage of 200 kV. X-ray photoemission spectroscopy (XPS) was recorded on a VG MultiLab 2000 system with a monochromatic Al $K\alpha$ source operated at 300 W. Inductively coupled plasma (ICP) data for Pt was obtained using an Optima 7300 DV instrument.

2.4. Electrocatalytic activity measurements

All the electrochemical measurements were carried out at room temperature in a conventional three-electrode cell using a Multipotentiostat (BioLogic, USA). 2 mg of as-prepared catalyst (or commercial Pt/C catalyst (10 wt% loading, Sigma-Aldrich)) was dispersed in 0.98 mL of isopropanol and 20 μL Nafion 117 solution (Sigma-Aldrich), followed by sonication till well-dispersed ink, and then 30 μL of the catalyst ink was spin-coated on $1\text{ cm} \times 1\text{ cm}$ carbon paper (Toray, Japan), and dried under room temperature. The prepared carbon paper was used as work electrode. Saturated calomel electrode (SCE) and platinum plate were used as reference and counter electrodes, respectively. All potentials in this work were converted to that of reversible hydrogen electrode (RHE) through RHE calibration described in literature [25,26]. In our system, $E_{\text{RHE}} = E_{\text{SCE}} + 0.272\text{ V}$.

Before the electrochemical measurement, the electrolyte (0.5 M H_2SO_4) was degassed by bubbling with high-purity N_2 for 30 min. The polarization curves were obtained by sweeping the potential from -0.7 to -0.2 V vs SCE, with a scan rate of 5 mV s^{-1} . The data were recorded after applying a number of potential sweeps until being stable. The polarization curves were re-plotted as overpotential (η) versus log current ($\log J$) to get Tafel plots for assessing of the HER activities of investigated catalysts. By fitting the linear portion of the plots to the Tafel equation ($\eta = b \log(J) + a$), the Tafel slope (b) can be obtained. The accelerated stability tests were performed in N_2 -saturated 0.5 M H_2SO_4 solution at room temperature by potential cycling between -0.7 and -0.2 V vs SCE at a sweep rate of 100 mV s^{-1} for 1000 cycles. At the end of the cycles, the resulting electrode was used for HER polarization and CV curves at a sweep rate of 5 mV s^{-1} . All the polarization curves were corrected with iR-compensation.

3. Results and discussion

BCF aerogel was chosen as a support because the low-cost carbon nanofibers have advantages of high inertness in harsh electrochemical conditions, large surface area as well as good conductivity for intermediation transport. The purified wet BC pellicle with controllable thickness was first cut into small pieces (Fig. 1a), and then lyophilized to form dry BC aerogels (Fig. 1b) via freeze-dry process (Step 1 in Fig. 1). The dried BC aerogels were then loaded to pyrolyze under a high-purity N_2 atmosphere at 800°C for 2 h to form the BCF aerogels (Fig. 1c and step 2 in Fig. 1). Finally, the as-prepared BCF aerogels were put into ALD reactor chamber to deposit Pt nanoparticles according to our previous work (Step 3 in Fig. 1).

The Pt particles on BCF aerogels (Fig. 1d) were characterized by TEM and XPS. After high-temperature pyrolysis and ALD deposition process, the macroscopic volumes of BCF aerogels (photograph in Fig. 1a and d) and the nanofibers gradually shrink to about half of their original size. However, the nanofibrous network structure of original BC precursors maintained well (Fig. 2a and b). As shown in Fig. 2a, the BCF composes of random-orientated carbon nanofibers. Detailed morphology images of the Pt particles grafted on BCF are shown in Fig. 2b and c. After only 5 cycles of low-nitrogen-filling ALD processes, the Pt particles are highly dispersed on the surface of carbon nanofibers, even in the inner central of BCF aerogel (Fig. 2b). The magnified TEM image (Fig. 2c) further demonstrates the dispersity of Pt particles. And the particle size distribution based on several TEM images is shown in the inset of Fig. 2c. It is presented that the average Pt particle diameter is 2 nm. The Pt loading on BCF is detected to be about 0.87 wt% by XPS analysis. The high-level of dispers and low-level of loading of Pt nanoparticles over high-surface-area 3D carbon networks is difficult to be achieved by normal Pt deposition process, allowing the feasibility to break the Pt loading limits for HER process.

Besides the weight percent calculation, the XPS spectroscopy of the Pt/BCF and bare BCF were performed in order to better elucidate the chemical structure of the grafted Pt nanoparticles. As shown in Fig. 2d, the Pt/BCF sample presents obviously Pt 4f_{5/2} and Pt 4f_{7/2} peaks, both of them are fitted well with the Pt^0 , confirming the presence of Pt [23,27]. However, the comparison bare BCF sample does not show Pt 4f peaks.

The electrocatalytic performance of the Pt/BCF was investigated in 0.5 M H_2SO_4 solution with a typical three-electrode system for HER. The catalytic performance of the bare BCF and the commercial Pt/C electrodes were tested for comparison. As shown in Fig. 3a, the Pt/C catalyst shows a distinctly high HER catalytic activity, with a very low overpotential (-19 mV) as H_2 evolution ($J = 10\text{ mA cm}^{-2}$), near to zero overpotential. The bare BCF presents almost negligible

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