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Platinum nanoparticles deposited nitrogen-doped carbon nanofiber derived from bacterial cellulose for hydrogen evolution reaction

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ABSTRACT

The nitrogen-doped carbon nanofiber derived from low and high proportion polyaniline doped bacterial cellulose (BC) was obtained via polymerization followed by pyrolysis. The resulting products were named LN-BC and HN-BC accordingly. Platinum nanoparticles modified LN-BC and HN-BC was then prepared (Pt@LN-BC and Pt@HN-BC) via electrochemical deposition. The morphologies of LN-BC and HN-BC indicated that the BC lost its nanowire structure after polyaniline modification and pyrolysis under nitrogen atmosphere. Platinum nanoparticles with diameters ranging from 3 to 5 nm can be well dispersed in the HN-BC support. The HER performance of Pt@LN-BC and Pt@HN-BC was fully investigated. Electrochemical results showed that the Pt-based catalysts had better HER activity than the Pt free catalysts in acid, indicating the HER activity was mainly from Pt. Besides, Pt@HN-BC had better HER activity than Pt@LN-BC in acid, suggesting N-doping rate was an important factor in enhancing HER activity. And the 10Pt@HN-BC (deposition for 10 s) with 4.38 wt% Pt loading was the best HER catalyst among the Pt@HN-BC. The onset potential (@ -1 mA cm^{-2}) and overpotential (@ -10 mA cm^{-2}) of the 10Pt@HN-BC in 0.5 M H_2SO_4 is -18 and -47 mV, respectively. The corresponding Tafel slope was -35 mV dec^{-1}, which is quite comparable to that of Pt/C (10 wt%). The electrochemical double layer capacitance (C_{dl}) and turnover frequency (TOF) were estimated and presented in the work. Long-term stability test confirmed that the 10Pt@HN-BC had excellent stability, which was important for practical application.

Introduction

The ever-increasing dependence on fossil fuels results in lots of undesirable situations, such as climate change, water, soil and air pollution [1–3], which have become public concerns and attracted significant attention. As one of the renewable and clean energy sources, hydrogen has been endowed with solemn mission to be the prospective counterplans to

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traditional energy. Therefore, it is of great urgency to find the ways to harvest hydrogen. Among various methods, electrochemical induced hydrogen evolution reaction (HER) has been confirmed to be one of the most efficient approaches [4–7].

HER activity is mainly dependent on the HER catalysts. Therefore, researchers have paid lots of attention to prepare HER catalysts. The Pt-based or Pt-like noble metals [8–11], molybdenum-based (MoO_2, MoS_2, $MoSe_2$, MoP, Mo_2C etc.) [12–18], cobalt-based (Co_3O_4, CoS_2, CoP, $Co(OH)_2$ etc.) [19–22] and nickel-based materials ($NiSe_2$, NiFeP, NiS_2 etc.) [5,23,24] are the popular candidates for HER catalysts. Among all the HER catalysts, Pt-based materials are regarded as the highly active and effective catalysts. However, the scarcity results in the high price of Pt-based materials and finally hinders their wide applications. The promising strategies are further improving the Pt utilization efficiency and producing low Pt loading catalysts. From this view, an effective approach is to disperse Pt nanoparticles on supports with excellent electrolyte wettability, electrochemical stability and conductivity.

Nanocarbon materials, including carbon nanotubes [11,12], graphene oxide [25–28], hollow porous carbons [8] and carbon fiber cloth [29,30], have been explored as promising support to stabilize Pt nanoparticles, owing to their large surface area, excellent electrochemical stability and conductivity. For example, Chen et al. have used nitrogen-doped hollow porous carbon polyhedrons as support of HER electrocatalyst [8]. Jiang and coworkers have reported a Pt/nitrogen-doped graphene nanocomposite for the hydrogen evolution reaction [10]. As a member of nanocarbon-based family, bacterial cellulose (BC) with carbon nanotube-like structure has receiving more and more attention because it is a low-cost and eco-friendly biomass that can be easily obtained via microbial fermentation process. It has been confirmed that BC can be a good substrate or support to fabricate hierarchical nanostructures in our previous work [31]. However, the poor conductivity of BC hinders its further use as support of HER catalyst. The effective way to solve this problem is heteroatom doping. Various nitrogen-doped carbon nanofibers have been reported as the support of HER electrocatalyst with enhanced catalytic activity [18,25].

In this work, we introduced a nitrogen-doped carbon nanofibers support derived from BC using polyaniline as nitrogen source (abbreviated as LN-BC and HN-BC). The Pt modified LN-BC and HN-BC were then obtained simply via electrochemical deposition in a 0.5 M H_2SO_4 with 2 mM H_2PtCl_6 for various times. The HER activity of the obtained catalysts were fully investigated. The kinetics process and crucial parameters were estimated and presented.

Experimental section

The bacterial cellulose (BC) was bought from Hongqi Science and Technology Ltd (Guilin), moisture content was 96%. Hydrochloric acid (HCl), aniline (C_6H_7N, ANI), ammonium persulfate ($(NH_4)_2S_2O_8$, APS) and other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd unless otherwise stated. All the reagents were used as received.

Schematic of the preparation and application of 10Pt@HN-BC was summarized in Fig. 1. Before electrodeposition of Pt nanoparticles, nitrogen-doped carbon nanofiber derived from bacterial cellulose was obtained firstly. Generally, 10 g fresh and pre-cleaned BC was placed in an average of two beakers labeled A and B. Secondly, 75 mL HCl solution (1 M) poured into each beaker to immerse the BC. Then, 28 and 280 μL ANI were respectively added to A and B, stirring for 24 h to ensure ANI was fully absorbed onto BC. Next, another 75 mL HCl solution (1 M) containing different amounts (0.342 and 3.42 g) of APS (served as an oxidant for polymerization of ANI to PANI) were

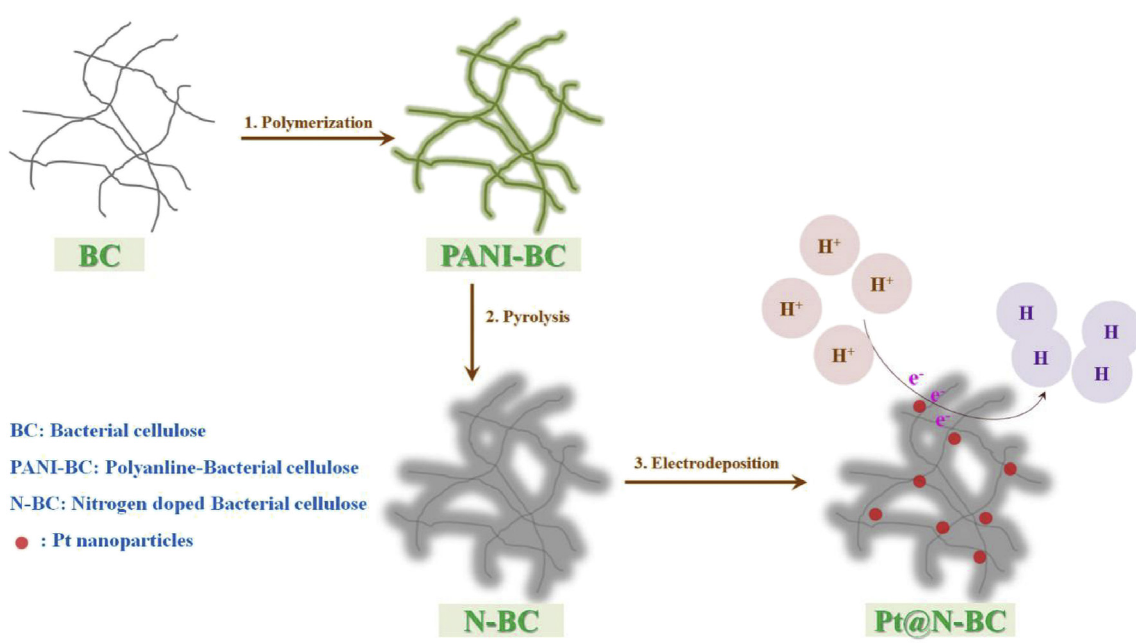

Fig. 1 – Schematic of the preparation and application of 10Pt@HN-BC.

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