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Short communication

A bioinspired approach to protectively decorate platinum–carbon for enhanced activity and durability in oxygen reduction

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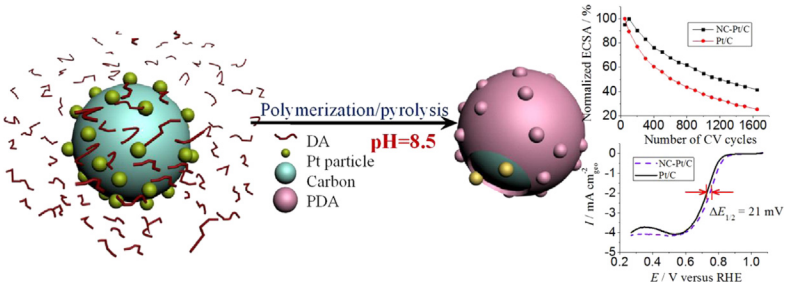
HIGHLIGHTS

- Pt/C was protectively decorated by DA self-polymerization and pyrolysis processes.
- Methanol tolerance of the NC–Pt/C catalyst was enhanced.
- NC–Pt/C still keeps 41.7% of its biggest ECSA after 1650 cycles.
- $E_{1/2}$ of NC–Pt/C for ORR was 21 mV more positive relative to Pt/C after cycles.
- Increased particle diameter in NC–Pt/C was markedly smaller than Pt/C after cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

This work develops a versatile and effective approach of protective decoration to improve the catalytic performance of nanostructured catalysts. The commercial platinum–carbon catalyst is decorated with polydopamine carbide via self-polymerization and pyrolysis processes. The electrocatalytic performance of the novel polydopamine carbide decorated platinum–carbon catalyst is characterized by voltammogram. Origin of improvement in its performance is analyzed by X-ray photoelectron spectroscopy and transmission electron microscope. It is exhibited that the catalytic activity and durability for oxygen reduction reaction and methanol tolerance of the polydopamine carbide decorated platinum–carbon catalyst are enhanced. The promoted effects result from the thermal treatment and decoration of polydopamine carbide which provides N species, slightly alters the Pt electronic structure and prevents Pt from agglomeration during long-term potential cycling.

1. Introduction

Carbon supported Pt (Pt/C) catalysts of the cathodes in direct methanol fuel cells (DMFCs) undergo dissolution and agglomeration during operation on account of low pH, high potential, high oxygen concentration and high relative humidity [1,2], bringing about decrease in Pt surface area and cathode catalytic efficiency [3]. One effective way to address this issue is decorating Pt/C with a

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protectant (e.g., a polymer or an oxide). For example, Pt/C was decorated with nafion during synthesis [4] or with polyaniline by induced polymerization in the presence of ammonium peroxodisulfate at a low temperature (<5 °C) [5]. These two catalysts above exhibited enhanced stability after decoration. In order to drive organics to directionally polymerize and decorate the catalyst, reaction conditions need to be accurately controlled in many cases. Furthermore, many decorated noble metal catalysts were ignored to be assessed for their methanol tolerance [4–7]. However, this assessment is very important because cathode catalytic efficiency can also be decreased by methanol cross-over through proton exchange membrane (PEM) in DMFCs.

As a versatile adhesive in living nature, dopamine (DA) can very easily adhere to nearly all types of material surfaces via spontaneous adsorption and polymerization processes [8,9]. Formation of polydopamine (PDA) coating involves the step of oxidizing catechol to quinine, followed by polymerization in a sense reminiscent of melanin formation [9,10]. Owing to this versatile adhesive attraction, DA can be used to decorate Pt/C for enhanced stability. However, PDA is not absolutely stable in strongly acidic medium [9]. To overcome this defect, PDA should be converted into N-doped carbon (NC, PDA carbide) [11] by its pyrolysis in inert atmosphere. In this work, a novel PDA carbide-decorated Pt/C catalyst was synthesized via self-polymerization and pyrolysis processes. Methanol tolerance, oxygen reduction reaction (ORR) activity and ORR catalytic durability of the NC–Pt/C catalyst were investigated.

2. Experimental

2.1. Synthesis of catalyst

The NC–Pt/C catalyst was synthesized by self-polymerization and pyrolysis processes of dopamine on the commercial Pt/C catalyst (20 wt.%, Johnson Matthey). A typical preparation consisted of the following steps: 100 mg of the Pt/C catalyst and 25 mg of dopamine hydrochloride were dispersed in 100 and 40 ml of double distilled water under ultrasonic stirring, respectively. The dopamine hydrochloride solution was added dropwise to the Pt/C suspension above under magnetic stirring. After that, the pH of the mixture was adjusted to 8.5 by a 1.5 M of Tris–HCl solution.

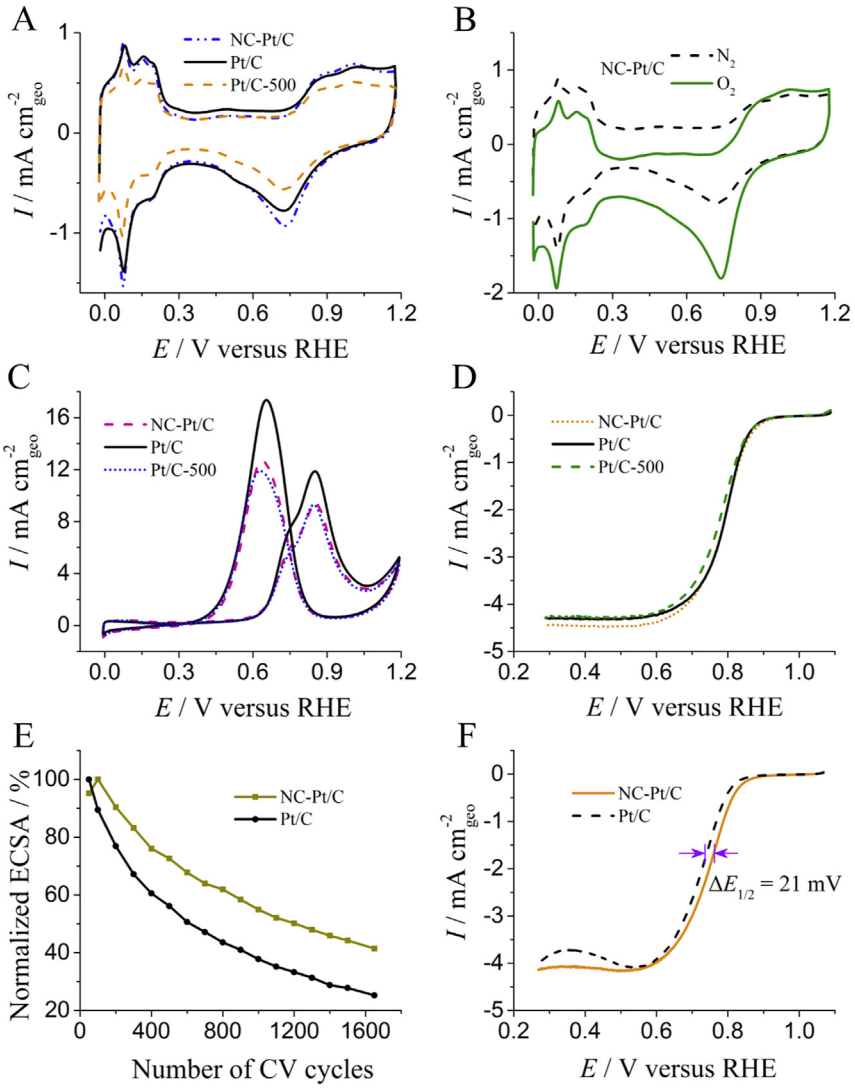

Fig. 1. (A) Cyclic voltammograms of Pt/C, Pt/C-500 and NC–Pt/C in N_2-saturated 0.5 M H_2SO_4; (B) Cyclic voltammograms of NC–Pt/C in O_2-saturated (solid lines) and N_2-saturated 0.5 M H_2SO_4 (dash lines); (C) Cyclic voltammograms of Pt/C, Pt/C-500 and NC–Pt/C in 0.5 M H_2SO_4 + 1 M CH_3OH; Rotating-disk voltammograms of the as-prepared catalysts in O_2-saturated 0.5 M H_2SO_4 at 1600 rpm before (D) and after (F) 1650 CV cycles in N_2-saturated 0.5 M H_2SO_4; (E) Normalized Pt ECSAs of the Pt/C and NC–Pt/C electrodes as functions of the number of CV cycles in N_2-saturated 0.5 M H_2SO_4. Cyclic voltammogram was conducted at 50 mV s^{-1}.