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Short communication

Amorphous ultra-dispersed Pt clusters supported on nitrogen functionalized carbon: A superior electrocatalyst for glycerol electrooxidation

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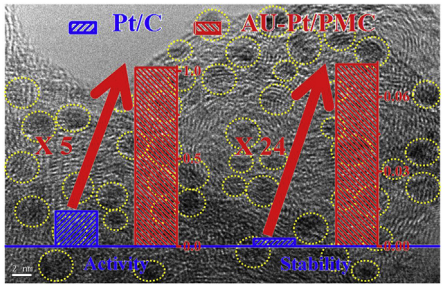
HIGHLIGHTS

- Amorphous ultra-dispersed Pt clusters anchor on PMC is developed.
- Pt loading of AU-Pt/PMC is striking low (5.6 wt%).
- As-obtained AU-Pt/PMC has superior activity and stability towards GOR.

GRAPHICAL ABSTRACT



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ABSTRACT

An amorphous ultra-dispersed electrocatalyst, AU-Pt/PMC, is successfully synthesized via severe etching process for glycerol oxidation reaction. What's appealing, it presents amorphous structure with ultra-small Pt clusters (0.36 nm) anchoring on nitrogen functionalized carbon support. Notably, the AU-Pt/PMC electrocatalyst takes on 5.1 times the activity and 24.3 times the stability compared with commercial Pt/C for glycerol oxidation reaction. The impressive electrocatalytic performance originates from the unique amorphous ultra-dispersed structure, as well as the superimposed effect between Pt clusters and Strong Metal-Support Interactions.

1. Introduction

To date, it is generally accepted that Pt-based electrocatalyst has been considered as the most active for glycerol oxidation reaction (GOR) in direct alcohol fuel cells (DAFCs) [1–4]. Notwithstanding, the prohibitive cost and scarcity severely hinder their widespread implementation. The resulting problem is how to lessen the Pt loading and thus reduce the cost of catalysts under the condition of maintaining good performance. Therefore, how to maximize the Pt mass activity and Pt utilization efficiency to gain affordable and sustainable electrocatalysts is a matter that admits of no delay.

To solve this problem, one effective route is to reduce the size of Pt particles [5]. Studies have shown, size reduction of metal particles benefits the performance of catalysts in two aspects: (i) As the particle size reducing, the exposed number of active sites on the small-sized particles increases significantly, it can increase the intrinsic activity of the catalyst; (ii) The surface atomic structure and surface defects will change, thus the number of unsaturated metal atoms will increase, so as to improve the catalytic activity [6–8].

Meanwhile, it is indeed crucial to maintain the stability while

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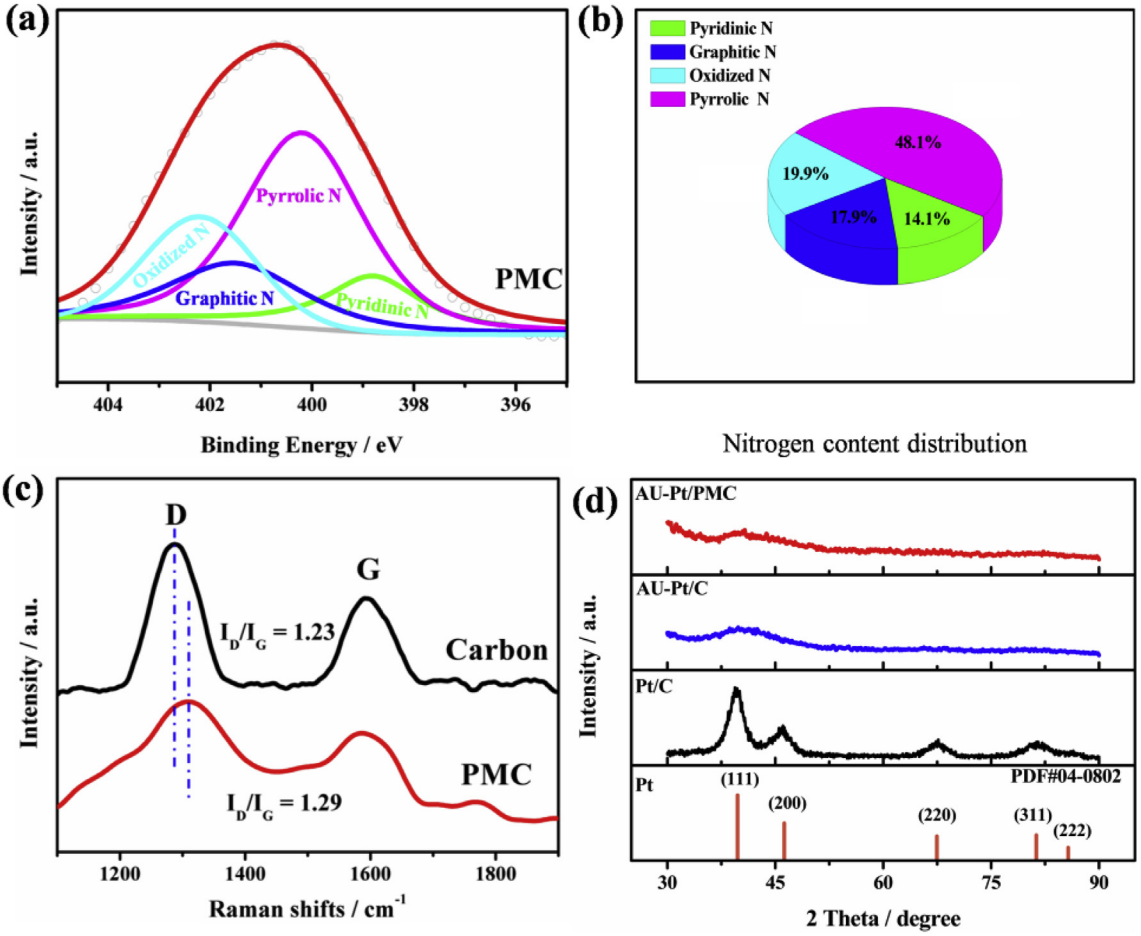

Fig. 1. (a) XPS spectra and (b) Nitrogen content distribution of PMC; (c) Raman spectra of PMC and Vulcan XC-72R carbon supports; (d) XRD patterns of AU-Pt/PMC, AU-Pt/C and Pt/C.

boosting the catalytic activity, in that ultra-small particles aggregate easily and will cause rapid activity decaying went through Pt oxidation, dissolution and Ostwald ripening during the prolonged operation [9,10]. If cut down the Pt loading and reduce the size of particle as well as make them anchored on the support well, the goal of increasing the activity and stability of the catalyst while reducing the cost will achieve.

Herein, we designed and synthesized an amorphous ultra-dispersed electrocatalyst, AU-Pt/PMC, which possesses high stability and low Pt loading. By taking a low-content Pt as a catalytic active component, cheap Fe as a sacrificial metal, formed alloy particles dissolving the sacrificial metal with acid etching treatment, and leaving the active component Pt clusters on the carbonized 1,10-phenanthroline modified carbon (PMC) [11] through its anchoring effect. Impressively, as-obtained AU-Pt/PMC electrocatalyst maximize the Pt mass activity and Pt utilization.

2. Experimental

2.1. Preparation of electrocatalysts

The $Pt_{0.1}Fe_{0.9}$/PMC precursor was prepared by a polyol reduction method [12]. The difference is that the used support is PMC. The preparation of PMC is consistent with the literature [11]. Whereafter, the $Pt_{0.1}Fe_{0.9}$/PMC precursor was etched by 3 M HCl for 12 h, through washing (high-purity water and ethanol) and drying (50 °C, 4 h) in turn. The amorphous ultra-dispersed catalyst was obtained, which was denoted as AU-Pt/PMC (5.6 wt% Pt loading). Besides, AU-Pt/C (5.6 wt% Pt loading) catalyst was prepared by the same method for comparison. Discriminates against AU-Pt/PMC, the used support of AU-Pt/C is Vulcan XC-72R carbon black instead of PMC. And the commercial Pt/C was also used as reference (20 wt% Pt loading, J. M.).

2.2. Characterization

The Raman spectra (Lab RAM HR Evolution), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Transmission electron microscopy (TEM) and Electrochemical test details are the same as in the literature [12]. It should be noted that all currents mentioned in this work were normalized to the noble metal mass (Pt mass is 0.0022 mg of AU-Pt/PMC and AU-Pt/C, 0.008 mg of Pt/C catalyst) on the working electrode.

3. Results and discussion

Fig. 1(a) displays XPS spectrum of PMC. Upon deconvolution of the N 1s XPS signals, the binding energies about 398.8 eV (pyridinic N), 400.3 eV (pyrrolic N), 401.1 eV (graphitic N) and 403.2 eV (oxidized N) were corresponded [13]. As shown in Fig. 1(b), the content of pyridinic N, pyrrolic N, graphitic N and oxidized N is 14.1%, 48.1%, 17.9% and 19.9%, respectively. It confirms that there is abundant nitrogen exists in the PMC, and this nitrogen-rich support could not only stabilize the ultra-small Pt clusters, but also enhance the catalytic activity of Pt clusters through the Strong Metal-Support Interactions (SMSI) [14].

Raman spectroscopy is the standard technique to investigate the structure and graphitic degree of carbon material. It is clear that both