

Bottom-up design of nitrogen-containing carbon catalysts for the oxygen reduction reaction

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The oxygen reduction reaction ($\text{O}_2 + 4\text{H}^+ + 4\text{e}^-$, ORR) is a key reaction for fuel cells. Nitrogen-doped carbon materials have been reported to exhibit high electrocatalytic activity for the ORR as non-metal catalysts [1, 2] and high durability even under acidic conditions [3]. Nitrogen-doped carbon materials are thus one of the most promising candidates as alternatives to high-cost Pt catalysts for fuel cell applications. Recently, we have reported that the ORR active site was created by pyridinic nitrogen (pyridinic N, nitrogen having two NC bonds) based on the experiments using newly designed graphite (highly oriented pyrolytic graphite, HOPG) model catalysts with well-defined π conjugation and well-controlled doping of N species, where the specific activities per pyridinic N in the HOPG model catalysts are comparable with those of N-doped graphene powder catalysts. Thus, the ORR active sites in N-doped carbon materials are concluded as carbon atoms with Lewis basicity next to pyridinic N [4].

The next stage to develop active nitrogen doped carbon catalysts is design of highly dense pyridinic N with high specific activity. One promising method is bottom-up catalyst design, in which active conjugated molecules with pyridinic N are assembled on catalyst supports with high surface area. This kind of hybrid material can be next-generation catalyst, which will be utilized in cathode catalyst for fuel cell.

Here, we have prepared a model catalyst by deposition of pyridinic N containing molecules on HOPG. The selected molecule is a dinbenz[a,c] acridine (DA), which possesses one pyridinic N. The DA molecules were adsorbed on the HOPG surface by dropping the dichloromethane solution of DA at room temperature without further heating or pyrolysis. Scanning tunneling microscopy (STM) revealed that DA molecules form two-dimensionally ordered self-assembled structure on basal plane of HOPG surface (Fig. 1a), where the presence of the pyridinic N is identified by X-ray photoelectron spectroscopy (XPS) as shown in Fig. 1b. The self-assembled monolayer of adsorbed DA on HOPG (DA/HOPG) surface shows ORR activity (Fig. 1c), which is comparable to that of nitrogen doped carbon catalysts, in terms of specific activity per pyridinic nitrogen [4]. These results indicate that the adsorption of pyridinic-N containing carbon molecules is a promising way as the bottom-up design for fuel cell cathode catalysts [5].

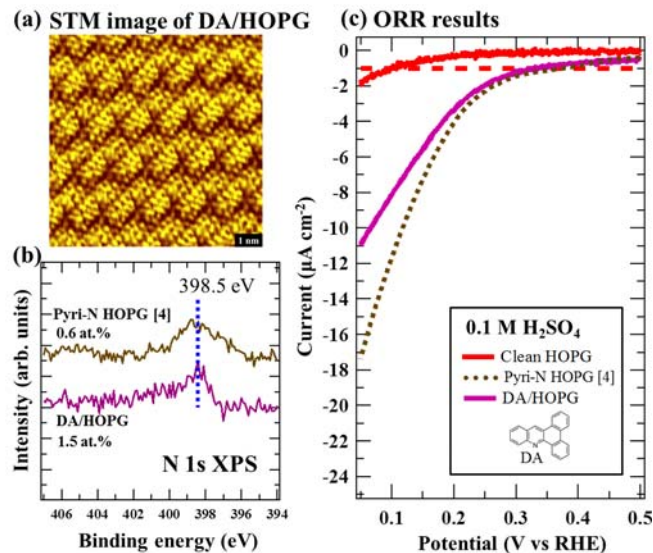


Fig. 1. (a) STM image of DA/HOPG, (b) XPS results, (c) ORR results.

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