# Preparation of the model electrode catalyst surface composed by nitrogen containing molecules on graphite surface

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## Abstract:

Pyridinic nitrogen species on nitrogen−doped carbon catalysts were recently found to create active sites for the oxygen reduction reaction (ORR). Bottom−up assembly of pyridinic−nitrogen−containing aromatic molecules on graphitic carbon electrodes is a promising synthesis method to design ORR carbon catalysts with a high density of active sites. Herein, we report the preparation and its evaluation of a model catalyst by dropping a solution of nitrogen-contained organic molecules onto a highly oriented pyrolytic graphite (HOPG) surface.

**Keywords:** Oxygen reduction reaction, nitrogen-doped carbon, scanning tunneling microscopy.

## 1. Introduction (11-point boldface)

Nitrogen containing carbon materials have been reported to show catalytic activities such as an oxygen reduction reaction ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$, ORR) in fuel cells. Among several types of nitrogen species in carbon materials, pyridinic nitrogen (nitrogen atom bound to two C atoms) was found to create ORR active sites in our previous work[1]. We then try to prepare catalytically active carbon surfaces covered with pyridinic nitrogen-containing aromatic molecules with high density. Quite recently, we have reported model catalyst studies using HOPG (highly oriented pyrolytic graphite) electrode covered with pyridinic nitrogen-containing aromatic molecules (dibenz[a,c] acridine (DA) molecule and acridine (Ac)molecule)[2]. The DA molecules form a two−dimensional ordered structure along the direction of the HOPG substrate by self−organization. Adsorbed DA on the HOPG surface shows high ORR activity in terms of specific activity per pyridinic nitrogen and is comparable to that of pyridinic−nitrogen−doped carbon catalysts. In this presentation, we will report these results with our preliminary obtained experimental results about other model catalyst system using different types of molecules.

## 2. Experimental (or Theoretical)

HOPG (ZYA grade, Panasonic Inc., 12 × 12 × 5 mm) was used as a graphite substrate to adsorb pyridinic-nitrogen-containing aromatic molecules. The HOPG was cleaved in air using scotch tape to clean the HOPG surface. The molecules such as $C_{21}H_{13}N$ (dibenz[a,c]acridine, DA) was first mixed with dichloromethane at room temperature, followed by ultra-sonication. Several microliters of the prepared mixture were then dropped onto the clean HOPG surface. After dropping the solution, the dichloromethane immediately evaporated at room temperature, leaving molecules on the HOPG surface. The prepared sample was then used for X-ray photoelectron spectroscopy and scanning tunnelling microscopy (STM) measurements.

## 3. Results and discussion

Figure 1 shows ORR results for model catalysis. One is HOPG as a reference sample; others are HOPG covered with pyridinic nitrogen molecules (Ac/HOPG and DA/HOPG) and HOPG with incorporated pyridinic nitrogen (pyriN HOPG [1]). Both ORR activities of DA/HOPG and Ac/HOPG are superior to that of pristine HOPG, indicating that ORR activity was improved by adsorbed molecules. Among them, ORR activity of DA/HOPG is almost comparable to that of pyriN HOPG. Quantitatively, the specific activity per pyridinic nitrogen atom was estimated to be 0.08 (e sec$^{-1}$ pyriN$^{-1}$) at 0.5 V vs RHE for DA/HOPG, which is comparable to that for pyridinic nitrogen incorporated graphene sheets (0.07 ~ 0.14 (e sec$^{-1}$ pyriN$^{-1}$))[1].

The structure of the adsorbed DA molecules on HOPG was examined with atomic resolution using STM. As shown in Fig. 2a, well-ordered patterns were clearly observed over the entire DA/HOPG surface. The result indicates that the adsorbed DA molecules formed a long-range, self-assembled adsorption structure on HOPG. The adsorption structure of DA derived from the careful analysis[2] is shown schematically in Fig. 2b. Figure 2c shows an STM image of a DA molecule on HOPG, which consists of several bright spots. These spots may be ascribed to the molecular orbitals of the DA molecule, because STM images generally reflect the local density of states of the sample surface. Since the STM image of Fig. 2c measured at −95 mV visualized the occupied states near the Fermi level, we compared this image with the highest occupied molecular orbital (HOMO) of a DA molecule calculated by Gaussian (Fig. 2d). The STM image resembles the calculated HOMO of the DA molecule in terms of size and shape of the orbitals, indicating that the DA molecules are adsorbed on the HOPG surface with a flat configuration, as schematically shown in Fig. 2e. However, the size, shape, and number of bright spots in Fig. 2c are not completely consistent with the calculated HOMO of DA (Fig. 2d), suggesting that the local electronic states of the DA molecule are modified by interfacial interactions between the DA molecules and the graphite surface.

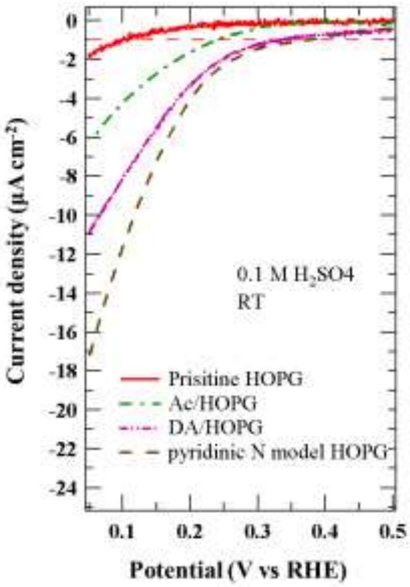

**Figure 1.** ORR results for model catalysts.

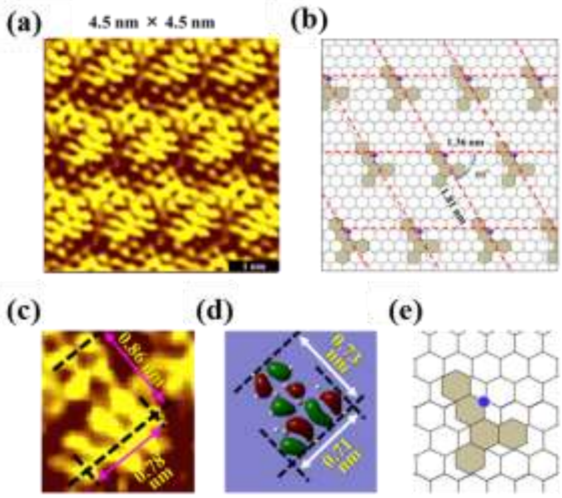

**Figure 2** (a) STM image of the DA/HOPG surface ($V_s$ = -95 mV, $I_t$ = 3.1 nA). (b) Model structure of DA/HOPG. (c) Magnified STM image of the DA molecule on HOPG. (d) HOMO of isolated DA calculated using Gaussian. (e) Magnification of the DA molecule in the model structure in Fig. 2b.

## 4. Conclusions

Using a bottom-up method, a model catalyst consisting of DA molecules adsorbed on a HOPG surface was prepared as a new type of nitrogen-containing carbon catalyst. The DA molecules adsorbed on HOPG showed ORR activity comparable to that of previously reported nitrogen doped carbon catalysts in terms of specific activity per pyridinic nitrogen. The DA molecules formed a self-assembled monolayer without stacking of molecules or aggregation.

## References

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