Active sites of nitrogen-doped carbon materials for oxygen reduction reaction

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Nitrogen-doped graphitic carbons as non-Pt catalysts for oxygen reduction reaction (ORR) have been paid much attention in recent years because commercialization of fuel cells requires less expensive and abundant catalytic materials. Identification of the active site of nitrogen-doped carbon materials for ORR is thus urgently required, but still under debate. Currently, the debate focuses on whether the active site is created by pyridinic N (N bonded to two carbon atoms) or graphitic N (N bonded to three carbon atoms, also called substituted N or quaternary N). To determine the active site conclusively, we prepared model catalysts of highly oriented pyrolytic graphite (HOPG) with pyridinic N (pyri-HOPG) or graphitic N (grap-HOPG). The active sites and adsorption properties were examined by ORR and post-ORR X-ray photoelectron spectroscopy (XPS). We have thus determined the active nitrogen species in carbon [1].

The graphitic-N doping was performed by mild bombardment with a nitrogen ion beam. To prepare the pyri-HOPG samples, edge patterning was first performed by bombarding the sample with an Ar^+ ion beam through a slit-patterned Ni mask as shown in Fig.1 A-D. The edged HOPG samples were then exposed to NH_3 at 973 K. The catalytic performances of the model catalysts were measured by cyclic voltammetry (CV) in acidic electrolyte (0.1 M H_2SO_4). It was found that the pyri-
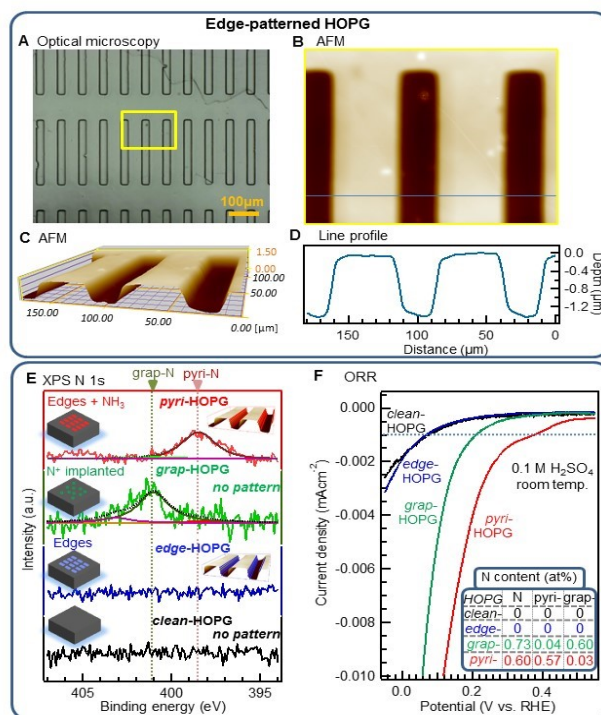

Figure.1 Structural and elemental characterization of four types of N-HOPG model catalysts and their ORR performance. (A) Optical image of patterned edge-N^+-HOPG. (B) The AFM image obtained from the region indicated by the yellow rectangle in (A). (C) 3D representation of (B). (D) Line profile of the AFM image obtained along the blue line in (B). (E) N 1s XPS spectra of model catalysts. (F) ORR results for model catalysts corresponding to (E). Nitrogen contents of the model catalysts are shown as inset in (F).

HOPG model catalyst shows high activity at high voltages, compared to the very low ORR activities of the N-free model catalysts (Fig.1 E, F). The pyri-HOPG sample with lower N concentration (N: 0.60 at%) is much more active than the grap-HOPG sample with higher N concentration (N: 0.73 at%). Since the pyri-HOPG sample is nearly free of graphitic N, the ORR results indicate that it is pyridinic N rather than the graphitic N that reduces the ORR overpotential and creates the active site. It is thus concluded that the ORR active sites in nitrogen-doped carbon materials are created by pyridinic N.

REFERENCES

[1] D. Guo, R. Shibuyaa, C. Akiba, S. Saji, T. Kondo, J. Nakamura, Science, 351 (2016) 361.