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High porosity nitrogen and phosphorous Co-doped carbon nanosheets as an efficient catalyst for oxygen reduction

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ABSTRACT

High porosity nitrogen and phosphorous co-doped carbon nanosheets with high surface area (1057.9 m^2 g^{-1}) are fabricated by using polyacrylonitrile and red phosphorous as the precursors. The catalyst exhibits outstanding catalytic performance towards oxygen reduction reaction (ORR), with its half-wave potential 35 mV more superior to that of Pt/C. In addition to high ORR performance, our catalyst also exhibits remarkable methanol tolerance, outstanding stability, as well as high catalytic efficiency (almost 100% selectivity towards four-electron path). Based on the characterization results, we find that moderate P introduction can significantly modify catalysts N compositions, as well as porous structures, which, we suggest, should be the proper origins to our catalyst's outstanding performance.

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Introduction

Exploring low-cost and highly efficient oxygen reduction reaction (ORR) electrocatalysts to replace Pt is highly important for the commercialization of advanced energy systems [1–11], e.g. proton exchange membrane fuel cells (PEMFCs) [12–14], direct methanol fuel cells (DMFCs) [15–17], and metal-air batteries [18–20], etc. Thanks to their low-cost and relative high ORR performances, doped carbons have been regarded as attractive candidates. The past several years have seen the great progresses in this field [21–23]. Unfortunately, these catalysts still fail to meet practical demands, however.

For carbons, hetero-doping (e.g. N, B, S, P, etc.), especially N doping, can modify their charge distribution, and enhance their ORR performance as a result. Compared with single doping, multi-element codoping was found to be more efficient in enhancing carbons' ORR catalytic performance due to the synergetic effect between different heteroatoms [24,25]. And among those heteroatoms, phosphorus has successfully attracted intense attention for its high electron-donating ability, strong synergetic effect with N dopants [26–29], as well as the ability to promote carbonization during the annealing procedure [27], which is expected to improve the

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electrical conductivity of carbons and facilitate their catalytic performance eventually.

In addition to charge distribution, well-define porous structures is another key factor for ORR performance enhancement [30–34], which is essential for both active sites expositions and mass transfer during the ORR procedures.

Therefore, N and P co-doped carbons, with rational porous structures, as well as high surface areas, can be expected to achieve outstanding ORR performance.

Based on these considerations, we develop a high porosity N and P co-doped catalyst with a rather high surface area (1057.9 m^2 g^{-1}) from polyacrylonitrile (PA) and red phosphorus. As expected, the catalyst exhibits outstanding ORR performance, with a half-wave potential 35 mV more positive than that of commercial Pt/C catalyst.

Experimental

Preparation of catalysts

The preparation procedure of catalysts is as illustrated in Fig. 1.

Briefly, 29.4 g (0.1 mol) trisodium citrate dihydrate (TCD),13.6 g (0.1 mol) zinc chloride ($ZnCl_2$) and 200 mL deionized (DI) water were first placed in a three-neck flask. After the solids were completely dissolved under vigorous stirring, 100 mL 2 M hydroxide sodium (NaOH) solution was added dropwise to afford a milk-like suspension. Then the flask was purged with pure N_2 and 8 mL acrylonitrile (AN) was added before the temperature was raised to 70 °C. The polymerization reaction was continued for 6 h after trace amount of ammonium persulfate (APS) was added, which was then filtrated and dried at 100 °C, during which the as-formed $Zn(OH)_2$ decomposed into ZnO. The obtained precursor was then grounded and named as "ZP", where "Z" and "P" refer to ZnO and polyacrylonitrile, respectively.

1.0 g ZP and 5.0 g red phosphorus were milled and mixed sufficiently in a mortar. The obtained powder blend was then programmingly heated and pyrolyzed at 900 °C for 1 h in a N_2 flow, followed by leaching with dilute sulphuric acid, washing with DI water and drying in vacuum. The obtained catalyst was labelled as "ZPAC-5P", where the number "5" indicates the mass ratio between used phosphorous and ZP. Catalysts with different P contents were also prepared through the same procedure and named as "ZPAC", "ZPAC-3P", "ZPAC-7P", respectively. For comparisons, the catalyst directly pyrolyzed from polyacrylonitrile (PA), without any ZnO addition, was also prepared and named as PAC.

Characterization

Scanning electron microscopy (SEM) images were obtained on a JSM-7100F field emission scanning electron microscope (JEOL, Japan), with an acceleration voltage of 5 kV. Transmission electron microscopy (TEM) was conducted on a JEM-2100 transmission electron microscope (JEOL, Japan) at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo-VG Scientific, USA). The nitrogen adsorption-desorption isotherms were recorded and analyzed by a Tristar II 3020 gas adsorption analyzer (Micromeritics, USA) using ultrapure N_2 as the adsorbate at 77.3 K.

Electrochemical measurements

The electrochemical measurements were conducted on a CHI 701E electrochemical workstation at room temperature (25 °C), couple with a rotating ring-disk electrode (RRDE, Gamry, USA) system. A glassy carbon electrode (GCE, 5 mm) was used as the working electrode substrate and a Hg/HgO/NaOH(1 M) and a Pt wire were used as the reference and counter electrode, respectively. For simplicity, the Hg/HgO/NaOH (1 M) electrode will be abbreviated as Hg/HgO. The potentials initially measured versus Hg/HgO were converted to the ones versus reversible hydrogen electrode (RHE) by adding 0.92 V.

Before every measurement, the GCE was polished on a microcloth and rinsed by DI water and dried under an infrared lamp.

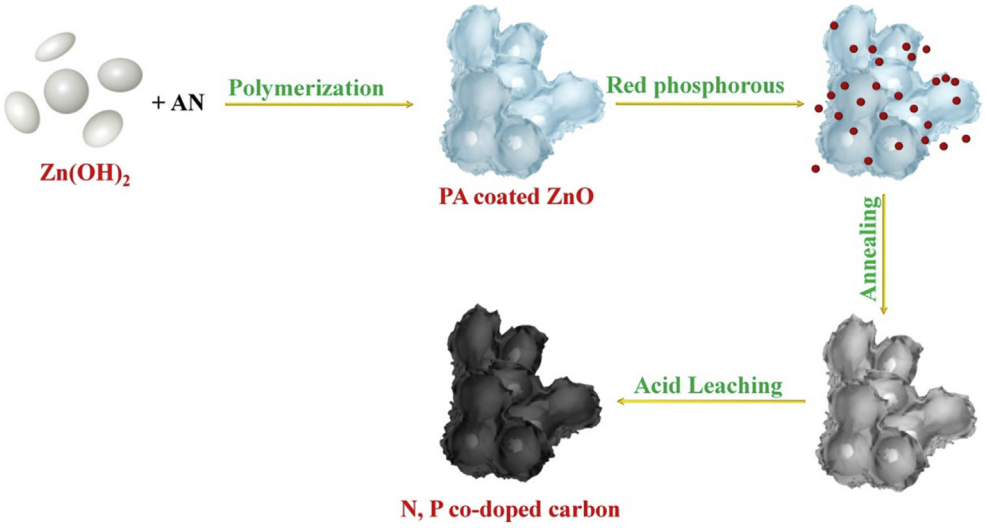

Fig. 1 – Schematic demonstration of the preparation of doped carbons.

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