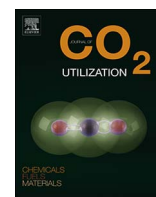




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In-situ boron and nitrogen doping in flue gas derived carbon materials for enhanced oxygen reduction reaction



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ABSTRACT

A model flue gas of N₂ and CO₂ mixture was directly converted into 'boron and nitrogen co-doped porous carbon materials (FlueBNPC)' at 500 °C and atmospheric pressure. The synthesized FlueBNPC showed enhanced electrocatalytic performance for oxygen reduction reaction (ORR) in the fuel cell cathode. Boron and nitrogen in the carbon network, which were simultaneously doped from flue gas in a single step, interplayed as active sites for the electrochemical reaction. The FlueBNPC showed higher electrocatalytic activity than previous heteroatom-doped carbon materials and comparable activity to that of a commercial Pt/C catalyst with a dominant four-electron transfer pathway. This enhancement originates from the newly formed B–N bonding combined with oxygen atoms in the carbon network. The synergetic effect of nitrogen attachment to the boron centre of the O–B–C bonds was investigated by DFT calculations. Our results indicate that flue gas itself can be used as an effective precursor for the one-step process not only to convert CO₂ into useful carbon materials, but also to insert boron and nitrogen atoms into the carbon lattices, and we demonstrate a potential utilization of the flue gas as a carbon source for electrochemical applications.

1. Introduction

Carbon dioxide (CO₂) is one of the major greenhouse gases that contribute to global warming and as such, much effort has been exerted to reduce the CO₂ emissions into the atmosphere. More than half of man-made CO₂ emissions are produced by fossil fuel combustion, which is essential for energy production [1]. Therefore, the proper management of flue gas, which contains 5–15% CO₂ and the rest, mostly N₂, is an important issue that needs to be resolved to mitigate the effect of climate change [2].

Given that CO₂ itself can be a cheap and sustainable carbon source for producing chemicals and carbon materials [3–6], there have been efforts to convert CO₂ into useful carbon materials like carbon nanotubes [7,8], diamonds [9], graphene oxides [10] and modified porous carbons [11]. However, most of the previously suggested carbon conversion processes require an additional step to separate CO₂ from the flue gas because pure CO₂ needs to be used as reactants. Since the separation of CO₂ from flue gas is one of the most expensive steps in carbon capture and sequestration, this study focuses on a novel method to utilize the flue gas itself. Recently, a heteroatom-doped carbon was synthesized directly from flue gas, and the carbon material was used for supercapacitors after additional chemical treatments of KOH [12]. Even

though that study suggested the potential of utilizing flue gas for producing BN dual-doped carbon materials, the mechanism for N-doping from flue gas is still unclear.

Thus, the current study proposes the mechanism of the nitrogen insertion into the carbon network during the reaction of flue gas with a reducing agent of NaBH₄. This mechanism will experimentally be confirmed by *in-situ* mass spectrometry and X-ray photoelectron spectroscopy (XPS). For further applications, the synthesized 'boron and nitrogen co-doped porous carbon (FlueBNPC)' will be used as an electrocatalyst for oxygen reduction reaction (ORR) in the cathode of fuel cells. Although Pt-based materials have been widely used for ORR due to their performance [13], the relatively high cost of Pt metal acts as the primary barrier preventing commercialization [14,15]. Subsequently, heteroatom (e.g. B and N)-doped carbon materials have been investigated as substitutes for Pt-based catalysts in the past [16–21]. Many previous works, which have attempted to explain the effect of BN co-doping on ORR, have concluded that hexagonal-BN (h-BN) is not efficient for enhancing ORR activity because sp² B–N covalent bonds are formed, which causes charge delocalization [22–24]. Unlike h-BN, isolate-doped B and N [22,23,25,26] or single BN pairs [24,27,28] have been suggested as effective active sites to promote ORR. Despite controversy surrounding the effective configurations of B and N atoms

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