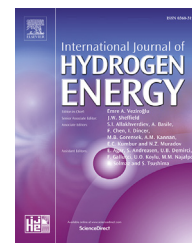




ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Direct synthesis of nitrogen-rich carbon sheets via polybenzoxazine as highly active electrocatalyst for water splitting

Periyasamy Thirukumaran ^{a,1}, Raji Atchudan ^{a,1},
Rukmanikrishnan Balasubramanian ^{a,1}, Asrafali Shakila Parveen ^{b,1},
Seong-Cheol Kim ^{a,*}

^a School of Chemical Engineering, Yeungnam University, Gyeongsan 38541, Republic of Korea

^b Department of Material Science and Engineering, Myongji University, Yongin, Gyeonggi-do 449-728, Republic of Korea

ARTICLE INFO

Article history:

Received 6 April 2018

Received in revised form

15 May 2018

Accepted 18 May 2018

Available online xxx

Keywords:

Polybenzoxazine

Nitrogen-rich carbon sheets

Electrocatalyst

Hydrogen evolution reaction

Water splitting

ABSTRACT

In this work, we propose a novel nitrogen-rich carbon sheets (N-CSs), with conceivable use as efficient catalysts for hydrogen evolution reaction (HER). N-CSs are directly synthesized from polybenzoxazine (PBz) by carbonization followed by KOH activation. PBz was prepared from eugenol, melamine, and paraformaldehyde through ring-opening polymerization. FT-IR and NMR spectroscopy confirmed the corresponding chemical structures of the new benzoxazine monomer. The morphology, structure and surface properties of the N-CSs are investigated by Raman spectroscopy, wide-angle X-ray diffraction, and X-ray photoelectron spectroscopy. The catalytic activity of N-CSs towards HER is thoroughly investigated by electrochemical techniques. In N-CSs, it is established that nitrogen gratified electrocatalytic activity, and hence nitrogen atoms should enhance the electrocatalytic properties by increasing the active sites. As the kinetic current is stabilized by the outer nitrogen atom as such, HER is proposed to proceed on these active sites by the Volmer-Heyrovsky mechanism. The N-CSs show outstanding catalytic activity towards HER with lowest onset-potential ($-10 \text{ mV}_{\text{RHE}}$) and Tafel slope (45 mV dec^{-1}) in $0.5 \text{ M H}_2\text{SO}_4$ aqueous electrolyte.

© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

To come across the task of diminishing fossil fuels, electrochemically renewable energy renovation and storage have been extensively researched. However, a replacement for insufficient and nondurable noble-metal electrocatalysts is

now essential [1,2]. Nowadays doping heteroatoms (e.g. N, S, P, B or others) into carbon is emerging as it can modify the physical and chemical properties of carbon to attract significant interest. More notably, this process can produce carbon-based materials with better ability to adsorb the atomic/molecular species undergoing catalytic reactions and without

* Corresponding author.

E-mail address: sckim07@ynu.ac.kr (S.-C. Kim).

¹ Authors contributed equally to this work.

<https://doi.org/10.1016/j.ijhydene.2018.05.108>

0360-3199/© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

substantially compromised conductive properties [3–6]. Nitrogen holding carbons can improve the properties of carbon for various applications including oxygen reduction reaction [7] oxygen evolution reaction [8] and photocatalysis. Doping N into carbon is important to tailor the electrocatalytic property such as oxidation stability, electrical conductivity, basicity and to alter the catalytic activity of carbon. But however, N-doped carbons as efficient catalysts for hydrogen evolution reactions (HER) have been rarely reported [9–14].

Hydrogen has demonstrated its potential as an energy carrier for high energy density applications and its production is environmentally friendly. Water splitting has been accomplished as one of the most effective methods to produce hydrogen at room temperature [15–18]. Today, Pt and its alloys provide a wide variety of available catalysts for HER under acidic condition to display the least overpotential [19–22]. However, the high cost and the deficiency of Pt raised great tasks to the large-scale production of hydrogen through the HER process. Many materials have been tested for HER in alkaline and acidic environments, including various combinations of metals, metal alloys [1,23,24], and more complex materials, sulfides, phosphates, carbides, and borides. Very recently, metal (Co, Mo, Ni)-encapsulated and heteroatom (N, S, P)-doped carbon signifies one new class of non-Pt catalysts for the HER. In general, the appropriate heteroatoms (N, S, P and etc.) doped carbon structure exhibits high ion diffusion efficiency due to the hydrophilic nature and this ion diffusion efficiency is a critical factor to decide the rate capability of water splitting including HER [25]. N-doping can dramatically increase the electrocatalytic activity of carbon. These catalysts display an invincible HER performance with the lowest onset-potential and outstanding stability [26–31].

Numerous methodologies have been reported for the synthesis of N-doped carbon materials, such as reactions of carbons with N-containing compounds, carbonizations with nitrogen-containing materials or through carbonizations of raw materials containing N atoms [32]. Recently, the preparation of N-doped carbon involves N-containing polymers like polyaniline, polypyrrole, polyacrylonitrile, polyindole as carbon precursors. A new class of thermosetting polymers: polybenzoxazines containing N atoms, display high char yields and high thermal stability, with the attraction of flexible molecular design. Still, only a few reports describe the preparation of polybenzoxazines as carbon precursors [33]. Polybenzoxazines are newly developed thermosetting phenolic resins, are deliberated to be one of the suitable starting material for the synthesis of N-rich carbons. The chemistry of benzoxazines is responsible for a number of inherent processing advantages, including molecular design flexible, no harsh catalyst required, near zero shrinkage, no volatile release during cure and low melt viscosity. Based on benzoxazine chemistry, it is a molecule having a benzene ring fused to another six-membered heterocycle containing one oxygen atom and a nitrogen atom. It is responsible to produce polymer nanostructures via strong hydrogen bonds. After thermally induced ring-open polymerization, in addition, the existence of stable intramolecular 6-membered-ring hydrogen bonding in the main chain of polybenzoxazine might avoid the destruction of the nanostructures. Therefore, it is potential to form nanostructures in the resulting carbon

materials from polybenzoxazine by a soft-templating method [34–36].

In this work, we report for the first time the synthesis of N-rich carbon via polybenzoxazine in combination with KOH chemical activation. At first, a new benzoxazine monomer with high thermal stability was prepared from eugenol, melamine and formaldehyde via a solution method. Then, it was proceeded with ring opening polymerization to form polybenzoxazine network with nitrogen and oxygen functionalities in the benzoxazine via hydrogen bonding. After polymerization, the material undergoes carbonization at 600 °C and KOH activation to obtain high nitrogen content. Electrocatalytic analyses expose electrocatalytic HER performance dominated by the intrinsic electronic structures of carbon electrocatalysts. The HER catalytic activity of the obtained material (N-CSs) and bare Pt plate has been comprehensively investigated.

Experimental

Materials

Eugenol and paraformaldehyde were purchased from Sigma-Aldrich (USA). Ethanol, melamine, potassium hydroxide (KOH), N-methyl-2-pyrrolidone (NMP), sulphuric acid (H₂SO₄), polyvinylidene fluoride (PVDF), and sodium hydroxide (NaOH) were purchased from Duksan Chemicals Co., Ltd. Republic of Korea. Plain carbon cloth (bare CC) was purchased from FuelCellsEtc (USA). All chemicals were used without further purification.

Synthesis of N-rich carbon sheets via polybenzoxazine

Melamine (6.3 g) and formaldehyde (9 g) were taken in a 500 mL three-necked round-bottomed flask fitted with a reflux condenser and magnetic stirrer. 200 mL of ethanol was added to the mixture and heated to 80 °C for 1 h. Eugenol (24.6 g) was dissolved in 100 mL absolute ethanol and then this solution was added dropwise into the reaction mixture and heated under reflux at 100 °C for 12 h. After cooling to room temperature, the reaction mixture was poured into 1 L of 1 M aqueous NaOH. The precipitate formed was collected by filtration, washed several times with water. After drying at 60 °C in a vacuum oven, pale yellow powder of benzoxazine was obtained, denoted by EM-Bz (Eugenol and melamine-based benzoxazine monomer). The synthesized EM-Bz monomer was heated stepwise in an oven at 100, 150, 200 and 250 °C for 1 h, respectively. Then, the cured polybenzoxazine (PBz) was further carbonized under a nitrogen atmosphere by heating at 600 °C (600 °C was chosen as carbonization temperature, as only the carbon part of the polymer remains at this temperature) [34,35,37] for 5 h with a ramp rate of 1 °C min⁻¹. Then, the obtained carbonized substance was thoroughly varied in an aqueous KOH solution followed by heating at 120 °C, where water vanishes. The activation process was carried out at 600 °C for 1 h in a tubular furnace under nitrogen flow with a ramp rate of 5 °C min⁻¹ and the resulting material was denoted as N-CSs. The detailed synthesis procedure of the PBz and N-CSs is clearly shown in Scheme 1.

Download English Version:

<https://daneshyari.com/en/article/7705491>

Download Persian Version:

<https://daneshyari.com/article/7705491>

[Daneshyari.com](https://daneshyari.com)