

Boron nitride-based electrocatalysts for HER, OER, and ORR: A mini-review

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ABSTRACT: A reliable and efficient solution to the current energy crisis and its associated environmental issues is provided by fuel cells, metal–air batteries and overall water splitting. The heart reactions for these technologies are oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). Different supporters such as graphene, carbon nanotube, and graphitic carbon nitride have been used to avoid agglomeration of active materials and provide maximum active surface for these reactions. Among all the supporters, boron nitride (BN) gains extensive research attention due to its analogue with graphene and excellent stability with good oxidation and chemical inertness. In this mini-review, the well-known strategies (exfoliation, annealing, and CVD) used in the synthesis of BN with different morphologies for HER, OER and ORR applications have been briefly debated and summarized. The comparative analysis determines that the performance and stability of state-of-the-art electrocatalysts can be further boosted if they are deposited on BN. It is revealed that BN-based catalysts for HER, OER and ORR are rarely studied yet especially with non-noble transition metals, and this research direction should be studied deeply in future for practical applications.

KEYWORDS: boron nitride; electrocatalyst; hydrogen evolution reaction; oxygen evolution reaction; oxygen reduction reaction

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1 Introduction

Energy crisis and environmental pollution have attracted research attention based on exploration of clean energy conversion and storage technologies such as fuel cells, metal–air batteries and water splitting [1–2]. Among these

techniques, electrocatalytic water splitting, which consists of cathodic hydrogen evolution reaction (HER) and anodic oxygen evolution reaction (OER), produces pure hydrogen [3]. The oxygen reduction reaction (ORR) is at the heart of fuel cell [1]. Hydrogen is an alternate, renewable and sustainable energy source with high energy density which is deemed to be a promising energy source to resolve the energy crisis and environmental concerns [4–5]. Currently, Pt and RuO₂/IrO₂ are state-of-the-art electrocatalysts for ORR/HER and OER, respectively. However, their scarcity and high price hinder practical application. To develop efficient and cost-effective electrocatalysts, metal oxide and hydroxide for OER and metal chalcogenide, phosphide, nitride, selenide, and carbide for HER have been deeply studied [6–7].

Dispersion of catalysts on the surface of supporting materials in order to reduce agglomeration and provide the maximum active surface for catalytic applications is the most effective and promising strategy. In the last few decades, carbon-based materials such as graphene, carbon nanotubes (CNTs), and carbon black have been widely studied as catalyst supporters [8]. Among all the supporters, boron nitride (BN) consisting of two-dimensional (2D) layers of sp² bonded boron and nitrogen in alternate arrangement to give honeycomb-like structural lattice, as in graphene, has been given special attention as a supporter material with characteristic excellent porosity, low cost, large surface area, thermal conductivity, good semiconducting nature and electronic transport properties [9–11]. In addition, BN has shown exceptional anti-oxidation and/or anticorrosion and chemical inertness even in harsh experimental conditions which is strongly recommended to be used as the supporting material for active metal particles in electrochemical applications. More importantly, the bonding between boron and nitrogen provides good electronic interaction at the interface and unique chemical coordination environment for heteroatom of catalysts while their superhydrophobicity may enhance their electrochemical applications [12]. Thus, BN has been studied theoretically [13–24] and experimentally [25–30], and has been applied as a catalyst in the field of HER [31–34], OER [8,35], ORR [12,30,36], dye-sensitized solar cell (DSSC) technology [27], carbon dioxide reduction reaction [11], and nitrogen fixation to ammonia [28,37]. Research in the area of BN-based electrocatalysts for HER and OER is still in need.

The present mini-review provides a briefly summarized study on the preparation of BN and its catalytic

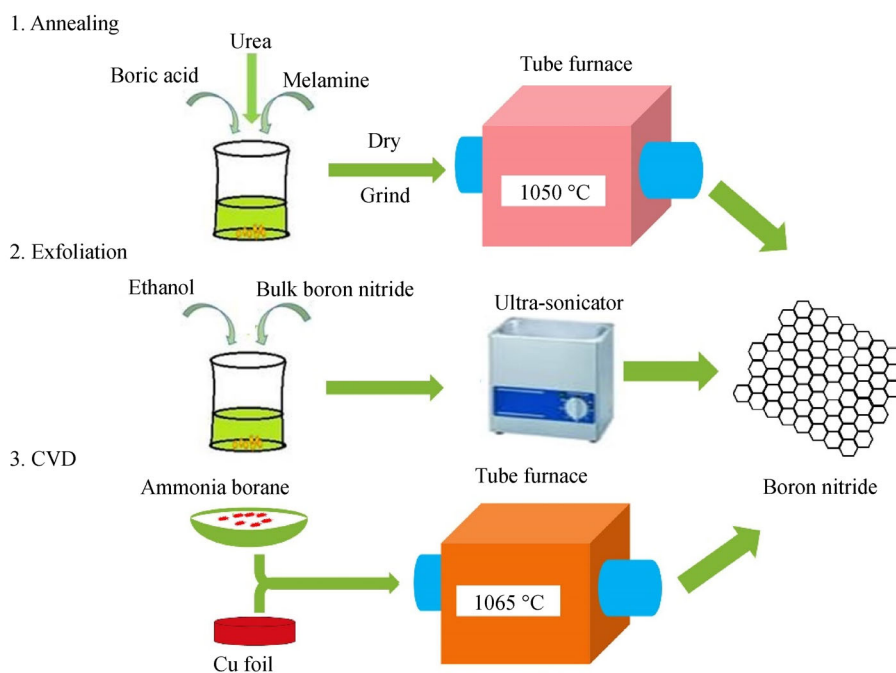
applications for ORR, HER and OER, as well as the relationship between its electrochemical applications and its morphology.

2 Synthetic approaches for BN-based electrocatalysts

The well-established and most reliable methods for the synthesis of BN that have been used in the field of HER, OER and ORR are annealing (calcination), exfoliation and chemical vapor deposition (CVD). The general synthetic scheme is shown in Scheme 1.

2.1 Annealing/calcination strategy for the synthesis of BN

Sun et al. used a solid-state calcination reaction method for the synthesis of BN. In that work, 1 g boron oxide, 2 g urea and certain weight of D-(+)-glucose were mixed and ground continuously for 2 h in agate mortar. The resulting materials were transferred to a tube furnace and heated at 1100 °C for 10 h with a temperature increasing rate of 10 °C·min⁻¹. The final product was washed with 0.1 mol·L⁻¹ HCl solution and water sequentially, followed by drying at 110 °C for 12 h to obtain carbon-doped BN. Similarly, BN was prepared without glucose and the as-prepared BN was decorated with copper and applied for the electrochemical application study [11]. In this work, the temperature is high and the time is long, thus it is very important to follow an energy-efficient strategy for the synthesis of BN. In this regard, Chen et al. followed a pyrolytic method to develop BN by adding 15 mmol of melamine to 50 mL of water and 30 mmol of boric acid was added to 20 mL of water at 90 °C with continuous stirring. A solution of boric acid was added to melamine under mechanical stirring for 30 min at 90 °C. The product obtained was filtered and dried at 70 °C to obtain melamine borate. About 2 g of urea, 1 g of melamine borate and 2 g of glucose were mixed, ground and annealed for 5 h at 1050 °C in an ammonia environment and finally washed with 0.1 mol·L⁻¹ HCl to obtain BN. Similarly, urea, glucose and boric acid with the ratio of 2:2:1 and urea, boric oxide and glucose with the ratio of 2:1:2 were used to prepare BN to compare electrochemical applications [33]. Cost effectiveness and kinetics are always debated in synthetic processes, therefore the development of a synthetic route with fast kinetics in terms of cost and time is highly recommended. Li et al. used a pyrolytic method to obtain BN. A mixture of melamine and boric



Scheme 1 Synthetic routes for the synthesis of BN.

acid with the ratio of 1:3 was added to water and stirred for 3 h at 90 °C. Then the solution was kept in an oven for 12 h at 60 °C to dry. The dried sample was heated in a nitrogen atmosphere for 4 h at 1050 °C to prepare BN which was decorated with active metal particles and was used for further application [36]. Similarly, Zhou et al. prepared BN via a calcination method with better time-saving step; 0.5 g boric acid, 1.02 g melamine, and 2.4 g urea were mixed and ground in a ball mill. The final mixed and ground materials were heated in a nitrogen environment for 3.5 h at a temperature of 1050 °C with the temperature increasing rate of 10 °C·min⁻¹. The BN was used as a supporter for bimetal phosphide and applied for further electrochemical applications [10].

In regard of energy crises, Liu et al. presented a further time and energy-saving step for pyrolytic strategy to synthesize BN. Urea and boric acid with the molar ratio 23:1 were added to pure water (40 mL) and heated up to 80 °C to evaporate water. The dried sample was heated for 6 h at 900 °C in a nitrogen environment to obtain carbon-doped BN which was further applied for the electrochemical application [28]. Similarly, Liu et al. used pyrolysis to prepare BN. Urea and boric acid with the molar ratio of 6:1 was dissolved in water to prepare a homogenous solution which was dried at 65 °C. The dried sample was

heated in a nitrogen environment for 5 h at 900 °C and then washed with HCl solution and water sequentially to get BN with a trace amount of carbon and oxygen. Similarly, NH₄Cl and H₃BO₃ as precursors were used for the synthesis of carbon-free BN, while NH₄Cl and NaBH₄ for carbon- and oxygen-free BN to compare application response [25]. One of the most energy- and time-saving pyrolytic strategies for the synthesis of BN is presented by Min et al. by dissolving urea and boric acid with the ratio of 3:0.1 in 5 mL of water and 5 mL of ethanol, and finally adding 0.2 g of polyether F127. The mixture was heated at 80 °C to recrystallize. The final product was heated in an argon environment for 2 h at 800 °C with the temperature increasing rate of 5 °C·min⁻¹ to obtain BN. The BN was decorated with active materials for the application study [29].

Patil et al. reported a two-step method to prepare BN. In the first step, a hydrothermal strategy was applied, and in the second step, the materials were freeze-dried and then annealed at low temperature to get the final materials. Powder (5 mg) of hexagonal BN (h-BN) was added to water (50 mL) via ultrasonication for 30 min at the frequency of 40 kHz to prepare a homogenous mixture. Then the material was transferred to Teflon-lined autoclave of 100 mL and heated for 6 h at a temperature 180 °C and

then washed with water. Subsequently the sample was freeze-dried and finally annealed for 2 h at 750 °C in a nitrogen environment [35].

2.2 Exfoliation strategy for the synthesis of BN

Exfoliation is the well-known and most studied method for the production of nanosheets of BN from their bulk morphology. Elumalai et al. applied an exfoliation technique for the synthesis of BN. Bulk BN ($3 \text{ mg} \cdot \text{mL}^{-1}$) was sonicated for 96 h in isopropyl alcohol (IPA) to exfoliate and get its sheets. The dispersion was centrifuged for 30 min at $3000 \text{ r} \cdot \text{min}^{-1}$ to collect the supernatant which was further diluted in IPA with the ratio of 1:3. The diluted dispersion of BN was filtered first using a $1 \mu\text{m}$ pore size filter and secondly by using a $0.45 \mu\text{m}$ pore size filter; the residue was again dispersed in IPA ($1 \text{ mg} \cdot \text{mL}^{-1}$) by ultrasonication for continuous 3 h and was then decorated with Au particles for the electrochemical application [30]. Similarly, Uosaki et al. used an exfoliation method to prepare BN by dispersing $3 \text{ mg} \cdot \text{mL}^{-1}$ of bulk BN in IPA followed by ultrasonication for 96 h in an ultrasonic box. The obtained material was centrifuged for 30 min at $3000 \text{ r} \cdot \text{min}^{-1}$ to collect the supernatant which was decorated with Au and studied for electrochemical application [34]. This method is highly time-consuming, and thus it is strongly recommended to follow a time-saving method. Kawrani et al. used an exfoliation method to develop boron nitride nanosheets (BNNS) from commercially available BN powder. Porcine skin gelatin (20 g) was dissolved in 80 mL of water at 75 °C. Then 1 g BN was mixed in gelatin solution and kept overnight in ultrasonic homogenizer at 50 °C at a pulse rate of $0.5\text{--}1 \text{ s}^{-1}$ and the amplitude of 65% for 3 h. Centrifugation at $6000 \text{ r} \cdot \text{min}^{-1}$ was used to collect exfoliated BNNS and then again dissolved to repeat the process several times. The final product was dried for 48 h at 80 °C and then calcined for 2 h at the heat rate of $5 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ and at a temperature of 600 °C to get pure nanosheets which were added with calcium copper titanium oxide for electrochemical applications [9].

The time used for exfoliation is still long and it is desirable to follow time-saving steps to prepare nanosheets of BN via exfoliation. Guha et al. used an exfoliation method to prepare BN in such a way that BN was added to dimethylformamide (DMF) in high-shear mixer at the shear rate of $5000 \text{ r} \cdot \text{min}^{-1}$ for 3 h to homogenize the mixture. The BN sheets were collected and further decorated with Pt for electrochemical applications [31].

Chen et al. used an exfoliation technique for the synthesis of BNNS which is a time-saving synthetic route. Bulk BN (1 g) was placed in a muffle furnace for 10 min at 800 °C and immediately transferred to liquid nitrogen to complete gasification. The sample was again transferred to the furnace and the same procedure was repeated five times. The final product was disseminated in IPA and ultrasonication was applied for 60 min, followed by centrifugation for 15 and 10 min at 1500 and $10000 \text{ r} \cdot \text{min}^{-1}$, sequentially. The final product was dried at 60 °C for an overnight in a vacuum oven. The BNNS was decorated with Pd for the application investigation [12]. Similarly, Zhang et al. used an exfoliation method to synthesize BNNS by dispersing 100 mg BN powder in ethanol (10 mL) and then exfoliating in an ultrasonic cell. The exfoliated sample was centrifuged at $6000 \text{ r} \cdot \text{min}^{-1}$ for 10 min to collect the materials and re-dispersed to repeat the process several times. The final product containing $0.6 \text{ mg} \cdot \text{mL}^{-1}$ of BNNS was collected which was further applied for electrochemical applications [37].

2.3 CVD strategy for the synthesis of BN

Liu et al. followed two steps. In the first step, a CVD method was used to obtain BN nanospheres from trimethoxyborane and ammonia. The nanoparticles (0.1 g) were dissolved in 10 mL of water and ultrasonicated for 5 min, and then in the second step, the sample was irradiated with a laser source at a wavelength of 1064 nm for 30 s. The width of pulse was set at 7 ns with a fixed voltage at 1064 nm/50% attenuation. The frequency was 15 Hz with the laser power of 260 mJ. IrO_2 and RuO_2 were deposited on BN for the study of the OER application [8]. Similarly, Liu et al. used a CVD method to develop BN on the surface of polycrystalline Cu foil. A solution of HCl and FeCl_3 with a ratio of 2:1 was used to polish Cu foil and then dried with nitrogen gas. The dried foil was placed in a tube furnace and annealed for 30 min at 1015 °C with gases of argon (260 sccm) and hydrogen (16 sccm). Then ammonia borane (1 mg) was placed upward and again heated for 60 min at a controlled temperature of 1065 °C. The prepared BN was deposited by metal as active materials for further applications [32].

3 Electrochemical applications of BN

3.1 ORR

ORR is the heart reaction of fuel cells and metal–air

batteries which are prime sources of energy conversion and storage in modern society [30]. In this regard, highly efficient catalysts are required for practical applications of ORR. Researchers have reported the use of BN-based catalysts for ORR. Li et al. used pyrolysis followed by hydrothermal method to prepare Pt-anchored porous BN (Pt/p-BN) electrocatalyst for the ORR application. The BN showed micro-sized rod-like morphology (diameter of 0.5–1 μm) with pores on their rods, and Pt nanoparticles were anchored on BN. The ORR activity of electrocatalysts was measured in 0.1 $\text{mol}\cdot\text{L}^{-1}$ HClO_4 saturated with O_2 at a rotating disk electrode (RDE) with the speed of 1600 $\text{r}\cdot\text{min}^{-1}$. The Pt/p-BN showed onset and half-wave potentials of 1.000 and 0.902 V which are more positive than those of the commercial Pt/C of 0.967 and 0.849 V, respectively. Similarly, the electrochemical specific surface area of Pt/p-BN (85.21 $\text{m}^2\cdot\text{g}^{-1}$ Pt) was higher than that of Pt/C (63.78 $\text{m}^2\cdot\text{g}^{-1}$ Pt). Pt/p-BN showed high durability and even after 10000 cycles only 2 mV changes occurred in half wave, as shown in Fig. 1 [36]. However, the scarcity and high price of Pt hamper its commercialization for renewable energy [22]. Thus, it is prime desire among the scientists to use other transition metal-based electrocatalysts; for example, Chen et al. prepared Pd-decorated carbon-hexagonal-boron nitride (h-BN/C/Pd) via exfoliation followed solvothermal and reflux techniques. The BN had nanosheet morphology and was covered with carbon and then decorated with Pd. The ORR performance was recorded in 0.1 $\text{mol}\cdot\text{L}^{-1}$ KOH solution using a typical RDE method. h-BN/C/Pd showed the half-wave potential of 0.91 V (*vs.* reversible hydrogen electrode (RHE)) which is higher than those of Pd/C (0.90 V) and Pd nanoparticles (0.89 V). The electrochemically active surface area (ECSA) values of h-BN/C/Pd, Pd nanoparticles and Pd/C were 288, 135 and 446 $\text{cm}^2\cdot\text{mg}^{-1}$ Pd, respectively. The durability of the electrocatalyst was excellent as it showed 10–12 mV decrease after 10000 cyclic voltammetry (CV) cycles [12].

In addition, gold has been studied to show that its nanoparticles are highly active in ORR. Thus, Elumalai et al. applied exfoliation followed by reduction to develop gold nanoparticles deposited on boron nitride nanosheets (AuNP-BNNS) as the ORR electrocatalyst. The rotating ring-disk electrode (RRDE) at 1500 $\text{r}\cdot\text{min}^{-1}$ with a speed of 10 $\text{mV}\cdot\text{s}^{-1}$ in solutions of 0.1 $\text{mol}\cdot\text{L}^{-1}$ HClO_2 and 0.05 $\text{mol}\cdot\text{L}^{-1}$ H_2SO_4 was used for the ORR study. The overpotentials of AuNP-BNNS/Au showed values of 720 and 760 mV (*vs.* RHE) at the current density of

0.2 $\text{mA}\cdot\text{cm}^{-2}$ in 0.05 $\text{mol}\cdot\text{L}^{-1}$ H_2SO_4 and 0.1 $\text{mol}\cdot\text{L}^{-1}$ HClO_4 , respectively. This performance is better than Pt which showed potentials of 830 and 860 mV under the same conditions. The electrocatalyst showed excellent durability even after 1000 cycles such that a reduction of only 10 mV was recorded [30]. BN exhibits fascinating application possibilities and properties and has been extensively studied. However, the availability of π electron of sp^2 hybridized materials exhibited free flowing feature which can be used in ORR directly [18]. Thus, Patil et al. used hydrothermal and annealing strategies for the synthesis of BNNS decorated with CNTs (CNTBN) for the comparison study of ORR. CNTBN was applied for ORR in 0.1 $\text{mol}\cdot\text{L}^{-1}$ KOH at the speed of 1600 $\text{r}\cdot\text{min}^{-1}$. The half-wave potential of CNTBN was 0.70 V (*vs.* RHE) at the current density of 4.7 $\text{mA}\cdot\text{cm}^{-2}$, which is higher than those of CNT (0.64 V) and h-BN (0.51 V). The sample also showed good onset potential of + 0.84 V *vs.* RHE while a 9 mV reduction was observed after 5000 cycles which confirmed their outstanding durability, even better than that of Pt/C which showed a decrease of 50 mV under the same conditions. The half-wave potential of CNTBN without annealing was 0.72 V (*vs.* RHE) which demonstrated the effect of annealing process on activity [35].

3.2 OER

OER is the key reaction in energy conversion and storage techniques such as fuel cells, metal-air batteries and water splitting. The most effective strategy for exercising OER is to increase the catalyst performance and reduce its cost in the context of supporting active materials on the surface of supporters with an objective of reducing agglomeration and exposing large active surface. In this regard, Liu et al. used a modified CVD method with laser therapy to prepare BN which was then decorated with IrO_2 by a simple deposition method using Nafion as the source of adhesion. The BN showed spherical morphology decorated with IrO_2 and used for the OER application. OER was studied in 1 $\text{mol}\cdot\text{L}^{-1}$ KOH solution with the sweep rate of 5 $\text{mV}\cdot\text{s}^{-1}$. IrO_2 , IrO_2/C and IrO_2/BN showed overpotentials of 285, 276 and 259 mV respectively at the current density of 10 $\text{mA}\cdot\text{cm}^{-2}$. Meanwhile, the Tafel slopes of IrO_2 , IrO_2/C and IrO_2/BN were 57.63, 56.92 and 36.68 $\text{mV}\cdot\text{dec}^{-1}$, respectively. After 12 h continuous uses, IrO_2/BN showed only 11 mV reduction in its overpotential which confirmed its stability for long-term application [8]. The addition of BN to the state-of-the-art electrocatalyst IrO_2 further

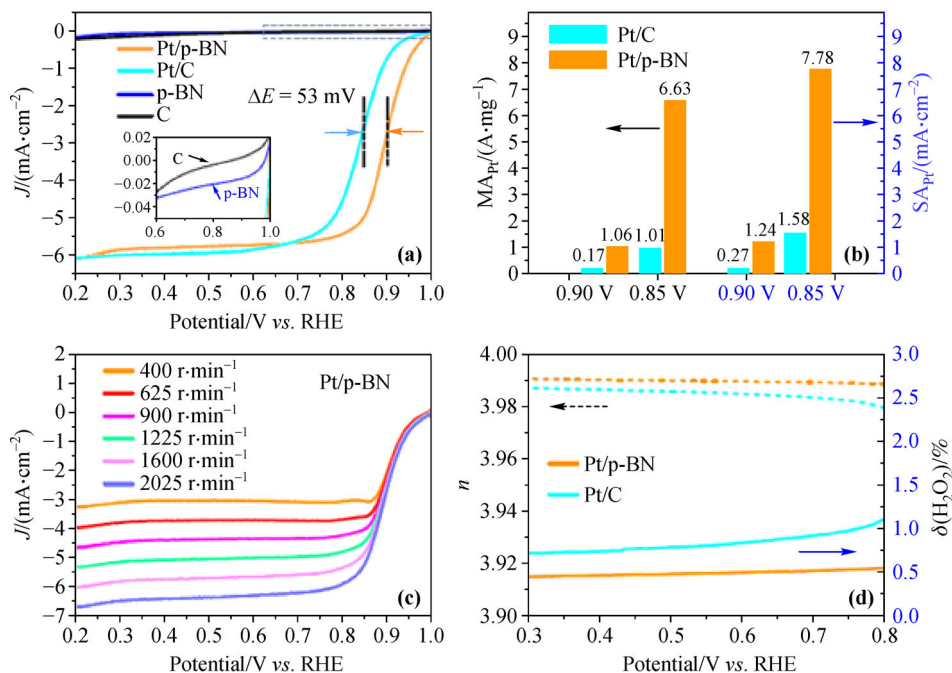


Fig. 1 (a) Linear sweep voltammetry (LSV) curves in O_2 -saturated $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ HClO}_4$ at a scan rate of $10 \text{ mV} \cdot \text{s}^{-1}$ and a rotating speed of $1600 \text{ r} \cdot \text{min}^{-1}$. (b) Mass and specific activities of Pt/p-BN and commercial Pt/C catalysts at 0.85 and 0.90 V . (c) LSV curves of Pt/p-BN in O_2 -saturated $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ HClO}_4$ at different rotation rates. (d) Corresponding electron transfer number (n , dot lines) and H_2O_2 yields ($\text{H}_2\text{O}_2\%$, solid lines) calculated from RRDE tests towards ORR on Pt/p-BN and commercial Pt/C in O_2 -saturated $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ HClO}_4$ electrolyte. Reproduced with permission from Ref. [36] (Copyright 2020, Elsevier B.V.).

enhanced its performance which demonstrated its role in OER. In addition, the prime desire of current research is to reduce the cost and improve the efficiency of electrocatalysts. In this regard, metal-free electrocatalysts have been studied for last few decades. Due to their unique structure and excellent electrical and chemical properties, CNTs along with BN showed tremendous catalytic features. As promising materials, BN-based CNTs are known as white graphene due to their analogous structure to graphene along with their special conduction because of their low porosity which arises from multilayers of boron and nitrogen. They have been considered good catalysts for OER. In this regard, Patil et al. used hydrothermal and annealing strategies for the synthesis of CNTBN for the comparison study of OER. CNTBN was applied in $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ KOH}$ solution at the speed of $10 \text{ mV} \cdot \text{s}^{-1}$ which delivered an onset potential of 0.38 V as well as an overpotential of 0.58 V (*vs.* RHE) at the current density of $10 \text{ mV} \cdot \text{s}^{-1}$, slightly higher than that of IrO_2 (0.46 V *vs.* RHE). In addition, the Tafel slope of CNTBN was $122 \text{ mV} \cdot \text{dec}^{-1}$ which is better than those of CNTs ($214 \text{ mV} \cdot \text{dec}^{-1}$) and Pt/C ($228 \text{ mV} \cdot \text{dec}^{-1}$), as shown in Fig. 2 [35].

3.3 HER

One of the most efficient strategies to prevent the corrosion of Pt is to wrap it with BN. In addition, theoretical studies have also confirmed that BN can modify inherent catalytic performance due to the modulation in the band structure. In this regard, Guha et al. followed exfoliation and reduction strategy to develop Pt-decorated h-BN nanosheets (Pt/h-BN) as an electrocatalyst for HER. The Pt nanoparticles were decorated on the surface of h-BN. The electrocatalyst was applied in $0.5 \text{ mol} \cdot \text{L}^{-1} \text{ H}_2\text{SO}_4$ at a speed of $10 \text{ mV} \cdot \text{s}^{-1}$ for the HER application. At the current density of $10 \text{ mA} \cdot \text{cm}^{-2}$, bulk Pt showed the onset potential of 0.07 mV and the overpotential of 0.128 mV (*vs.* RHE), while for Pt/h-BN, there were the same value of the onset potential and a smaller overpotential (0.118 mV *vs.* RHE). The Tafel slopes of Pt and Pt/h-BN were 34 and $29 \text{ mV} \cdot \text{dec}^{-1}$ with the exchange current densities of 0.47×10^{-4} and $0.43 \times 10^{-4} \text{ A} \cdot \text{cm}^{-2}$, respectively, as shown in Fig. 3 [31].

The performance of other noble transition metals can also be enhanced with BN as the supporter. Elumalai et al. used exfoliation and followed by a solvothermal method to

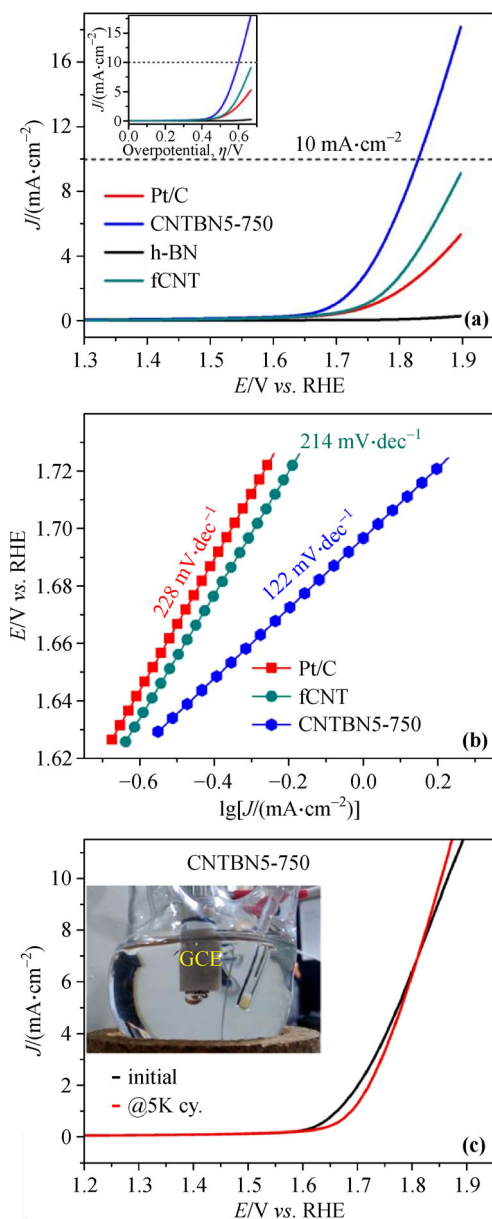


Fig. 2 (a) Comparative OER voltammograms of CNTBN5-750, bare h-BN, functionalized CNT (fCNT), and Pt/C catalyst, in $0.1 \text{ mol}\cdot\text{L}^{-1}$ KOH electrolyte at $1600 \text{ r}\cdot\text{min}^{-1}$ with the scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$; inset shows plot of current density versus overpotential (η) with respect to standard thermodynamic potential for OER. (b) Tafel plots of OER, extracted from polarization curve in panel (a). (c) Comparative anodic OER polarization curves for CNTBN5-750 before and after the durability test in $0.1 \text{ mol}\cdot\text{L}^{-1}$ KOH solution; inset shows photograph of oxygen bubble generated on the CNTBN5-750 modified electrode during OER. Reproduced with permission from Ref. [35] (Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

prepare Au deposited metal ($M = \text{Co}, \text{Cu}, \text{Ni}$) based BNNS on the surface of reduced graphene oxide (rGO) and Au (Au- M -BNNS/Au) as electrocatalysts for HER. The

HER application was studied at $1 \text{ mV}\cdot\text{s}^{-1}$ in the H_2SO_4 ($0.5 \text{ mol}\cdot\text{L}^{-1}$) solution, and Au-Ni-BNNS/Au was found to be an excellent electrocatalyst during the HER application. The overpotentials of Au-Ni-BNNS/Au were 16 and 30 mV at the current densities of 5 and $15 \text{ mA}\cdot\text{cm}^{-2}$, respectively, larger than those of the Pt electrode. Meanwhile, the exchange current densities for Au-Ni-BNNS/Au and Pt electrodes were 8.6×10^{-5} and $4.2 \times 10^{-4} \text{ A}\cdot\text{cm}^{-2}$ with the Tafel values of 36 and $30 \text{ mV}\cdot\text{dec}^{-1}$, respectively [26]. Uosaki et al. followed the same strategy for the preparation of Au-deposited BNNS. The synthesized materials were applied in $0.5 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 solution with a sweep rate of $1 \text{ mV}\cdot\text{s}^{-1}$ for the HER application. At the current densities of 5 and $15 \text{ mA}\cdot\text{cm}^{-2}$, the overpotentials of BNNS/Au were 30 and 40 mV, while those of Au were 350 and 430 mV, all higher than those of Pt, respectively. The exchange current densities of Au, BNNS/Au and Pt were 3.1×10^{-7} , 4.6×10^{-5} and $4.2 \times 10^{-4} \text{ A}\cdot\text{cm}^{-2}$ with the Tafel slopes of 75, 27 and $30 \text{ mV}\cdot\text{dec}^{-1}$, respectively. The stability of BNNS/Au was outstanding as its overpotential was increased only 20 mV after 3000 CV cycles [34]. Moreover, as the electrocatalytic activity can be tuned by the mixing of d_z metal orbitals with B- p_z and N- p_z orbitals, Liu et al. followed CVD and polymethyl-methacrylate (PMMA) methods to prepare copper- and gold-supported h-BN (h-BN/Cu and h-BN/Au) electrocatalysts for HER applications. The h-BN nanosheets with sizes of 5–12 and $5 \mu\text{m}$ were dispersed on the underlying Cu and Au supports, respectively. The HER data confirmed that h-BN/Cu delivered a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ at the overpotential of -0.688 V vs. RHE, while h-BN/Au demonstrated a current density of $900 \text{ mA}\cdot\text{cm}^{-2}$ at the same overpotential. The Tafel slope values for h-BN/Au and h-BN/Cu were 108 and $136 \text{ mV}\cdot\text{dec}^{-1}$ with the exchange current densities of 4×10^{-8} and $1 \times 10^{-6} \text{ A}\cdot\text{cm}^{-2}$, respectively. The performance of Au is higher than h-BN/Au and h-BN/Cu, as Au has a potential of 0.688 V vs. RHE with the current density of $1600 \text{ mA}\cdot\text{cm}^{-2}$, the Tafel slope of $130 \text{ mV}\cdot\text{dec}^{-1}$, and the exchange current density of $4 \times 10^{-6} \text{ A}\cdot\text{cm}^{-2}$ [32].

4 Conclusions

This article summarizes most applied strategies for the synthesis of BN for the electrochemical applications. Most of the researchers used calcination, exfoliation and CVD methods to produce BN as a supporter for active materials. The most common morphology of BN is nanosheet, which

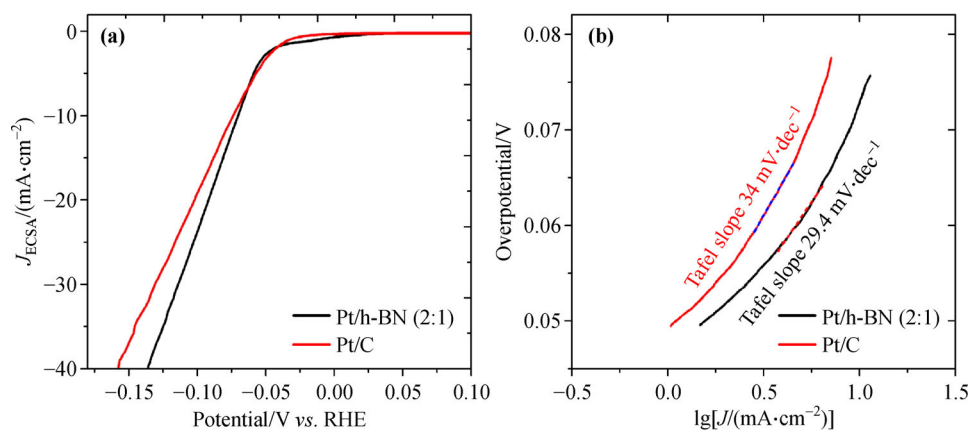


Fig. 3 (a) LSVs (scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$) and (b) Tafel slope analyses for Pt/h-BN (2:1) and Pt/C (20:80, commercial catalyst). The current densities in the plots are calculated using the ECSA. The fitted regions of the Tafel slope calculations in panel (b) are marked with dotted overlays. Reproduced with permission from Ref. [31] (Copyright 2018, American Chemical Society).

has high surface area and provides more opportunities for materials to be deposited in order to minimize their agglomeration. The main focus of previous studies on BN-based materials was to use it as a supporter for different materials to enhance their performance. It is confirmed that BN as a supporter can enhance the performance of active materials for HER, OER and ORR. The BN even boosted the electrochemical applications of Pt and IrO_2 with low overpotentials at high current densities. BN-supported Pt shows lower overpotential than commercialized Pt/C for HER. Similarly, BN-deposited Pt shows better half-wave potential than Pt for the ORR application. In addition, even the IrO_2 performance for OER can be further enhanced as it can be deposited on the surface of BN. The stability of BN-supported electrocatalysts for HER, OER and ORR is higher than that for other supporters and for the absence of supporters. BN-based electrocatalysts can further enhance the catalyst performance in order to lower the overpotential/half-wave potential with large current density and long-term stability. However, BN is rarely studied with other transition metals yet for electrochemical applications of HER, OER and ORR. Thus this area still needs to be further studied for practical applications.

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