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Recent developments of carbon-based electrocatalysts for hydrogen evolution reaction

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ABSTRACT

Development of effective technologies for clean and sustainable hydrogen energy has been attracting great attention. Toward this end, an effective and promising approach is based on the electrolysis of water for hydrogen production. To date, the most effective hydrogen evolution reaction (HER) electrocatalysts are Pt-group metals with a low overpotential to generate large cathodic current densities. However, the high cost and scarcity severely limit their broad utilization. As alternatives to Pt electrocatalysts, transition metal compounds as effective HER catalysts have been prepared in a series of recent studies. However, thus far, it remained a great challenge to develop highly active HER catalysts with a low overpotential based on earth-abundant and cost-effective materials. Recently, the new significant developments about carbon-based electrocatalysts with a low overpotential toward HER have stimulated a great deal of the researchers' interest. In particular, the catalytic activity of carbon based-catalysts can be enhanced by transition metal nanoparticles as core and nonmetal doping into carbon skeleton, which can modulate the electronic state density of carbon to produce new active sites for HER. In this feature article, we review the research progress in the development of carbon-based electrocatalysts toward HER in acid electrolytes throughout the past few years. In addition, some notable matters and challenge in the research of HER are discussed in this review.

Contents

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1. Introduction

Development of effective technologies for clean and sustainable hydrogen energy has been drawn increasing attention in the past few years, as hydrogen is hailed as a promising energy source to reduce our dependence on fossil fuels and benefit the environment by reducing the emissions of greenhouse and other toxic gases. Toward this end, an effective and promising approach is based on the electrolysis of water for hydrogen production. Electrocatalytic hydrogen evolution reaction (HER) preferably driven by solar energy is a highly attractive methodology for meeting these requirements [1–3]. Yet such a promise will be realized only when the production can be carried out in an efficient, low-cost, and environmentally friendly fashion. As shown in the equation: $H^+ + \text{catalyst} + e^- = \text{catalyst-H}$ (acid solution), the catalyst need only adsorb free H^+ ion in acidic electrolytes. But, as shown in the equation: $H_2O + \text{catalyst} + e^- = \text{catalyst-H} + OH^-$ (alkaline solution), the catalyst need break the H–O–H bonding in alkaline electrolytes before adsorbing H^+ ion. So, the acidic electrolytes (e.g. 0.5 M H_2SO_4) are preferred for water electrolysis to produce hydrogen as there are enough H^+ ions in the electrolyte to react on the electrode surface. In addition, hydroxide-conducting polymeric electrolytes are still in their technological infancy: they are unstable and less conductive than their proton-conducting counterparts and impose greater overpotentials for HER [4]. Therefore significant research efforts have been devoted to the design and engineering of acid-stable HER catalysts.

To date, Pt-based electrocatalysts are known to efficiently catalyze HER, while their widespread use has been limited by their low earth-abundance and high-cost; hence, the development of HER catalysts that are composed of inexpensive and earth-abundant elements has been one of the main targets in renewable energy research in recent years [5–9]. Molybdenum- and transition-metal-based compounds are an exciting family of HER catalysts, including MoS_2 [10–12], $MoSe_2$ [13], Mo_2C [14], MoP [15], WS_2 [16], $CoSe_2$ [17], CoS_2 [18], CoP [19,20], NiP [2], M_3C (M: Fe, Co, Ni) [21], which exhibit excellent activity and robust stability in acidic electrolytes. Recently, the studies about carbon-based catalysts with low overpotentials for HER have stimulated a great deal of interest. The pristine carbon materials are electrochemically inert or possess the poor catalytic activity [22–25]. This is the basis that we can use various carbon-based current collectors such as glassy carbon, carbon paper and carbon cloth in electrochemical experiments. Chemical modification of the carbon surface is usually necessary in order to enhance its electrocatalytic activity [26]. Actually, the electronic state density of carbon may be modulated by transition metal nanoparticles [22,27,28] and nonmetal doping [28–30], such that carbon may serve as active sites for HER. As a rising category of potential candidates for the replacement of Pt-based catalysts, carbon-based materials are considered to have great potential to solve some vital issues for HER. Up to now, there are two main kinds of carbon-based electrocatalysts: (1) nonmetallic elements doped carbon and (2) the metal@carbon core-shell structures. Recent rapid increases of carbon based electrocatalysts for HER have motivated demand for reviewing of this research field. To the best of our knowledge, although some investigations or reviews involving transition metal based, especially molybdenum-based compounds as HER catalysts have been reported [31–38], comprehensive reviews about carbon-based electrocatalysts for HER are still rare [39]. This review summarizes recent achievements in carbon based electrocatalysts for HER, and beneficial to future development of other novel low-cost catalysts with high activities and long lifetimes for practical applications. Additionally, some notable matters and challenge in the electrochemical measurement of HER are discussed in this review.

2. Nonmetal doped carbon for HER

Hetero-atoms (e.g. N, S, P, B or others) as dopant into carbon can modulate carbon's physical and chemical properties to obtain more reactive sites. More importantly, this process can produce carbon-based materials with improved ability to adsorb the atomic/molecular species undergoing catalytic reactions and without substantially compromised conductive properties [40]. These types of heteroatoms doped structures may provide opportunities for further developing low-cost metal-free catalysts with high activities and long lifetimes. It has been known that the difference in electronegativity and size between the hetero-atoms (N, P, B, and S) and carbon can polarize adjacent carbon atoms to facilitate oxygen reduction reaction (ORR) [41–43], which may be applicable to the hydrogen evolution process [24,28,44]. The HER performances of heteroatom-doped carbon metal-free catalysts are summarized in Table 1.

2.1. Nitrogen-doped carbon for HER

Nitrogen containing carbons have received increasing interest as they can improve the properties of carbon for various applications, including ORR [51] and photocatalysis [52]. When nitrogen atoms are introduced into the carbon structure, the electrical conductivity, basicity, oxidation stability, and catalytic activity of carbon can be altered. The performance of these materials crucially depends on the amount of nitrogen in the carbon host as well as its local structure. However, the N doped carbons as efficient catalysts for HER have rarely been reported [48,53,54]. Antonietti et al. [53] reported that the carbon nitride (C_3N_4) electrodes show high HER activity with low overpotential and acceptable current densities due to an enhanced H adsorption (Volmer step). Qu et al. reported that hierarchical architecture of graphitic carbon nitride (g-C_3N_4) nanoribbon-graphene provides a large accessible surface area, multi-electron transport channel and short diffusion distance for an excellent charge separation and transfer, that effectively accelerates the electrochemical process for HER [47]. As shown in Fig. 1, Qiao et al. synthesized a flexible three-dimensional (3D) film by integrating porous C_3N_4 nanolayers with nitrogen-doped graphene sheets, which can be directly utilized as