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Peer-reviewed version available at *Electrochem* **2020**; doi:10.3390/electrochem1020008

Graphene-based catalysts for hydrogen evolution reaction

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Abstract

Developing sustainable and renewable energy sources is critical as higher and higher global energy and environmental challenges arise. Hydrogen has the highest mass/energy density of any fuel and is considered one of the best sources of clean energy. Water splitting is regarded as one of the most promising solutions for hydrogen production on a large scale. Highly efficient, durable and cost-effective catalysts for hydrogen evolution reaction (HER) are critical in the realization of this goal. Among many materials proposed, graphene-based materials offer some unique properties for HER catalysis. In this review, we present recent progress on development of graphene-based electrocatalysts toward HER throughout the past few years.

Keywords: HER; Graphene; Catalysis; Catalysts; Electrolyser

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Introduction

Most of the energy produced worldwide comes from fossil fuels, which presents several problems. Firstly, combustion of fossil fuels produces carbon dioxide (CO_2) which drives on climate change [1]. Secondly, fossil fuels are not a renewable source and once the reserves are exhausted, another form of storing and producing energy will be needed.

In this scenario, water splitting appears to be the best method of converting electrical energy to hydrogen as it requires only water and produces nothing but pure hydrogen (H_2) and oxygen (O_2). In a typical water electrolysis system, H_2 is produced at the cathode through the hydrogen evolution reaction (HER) and O_2 is produced at the anode through the oxygen evolution reaction (OER) [2].

The overall reaction for HER occurs in the whole pH range in the subsequent way:

$$2H^{+} + 2e^{-} \rightarrow H_2 \qquad (\mathrm{pH} < 7) \qquad (1)$$

$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-} \qquad (\mathrm{pH} > 7) \qquad (2)$$

Pure hydrogen is a clean energy vector, which can be stored to obtain energy through fuel cell technology. In this way, the energy obtained by renewable energy sources (such as solar, wind, etc.) can be stored in hydrogen form delivering energy without producing any polluting waste when it is required [3]. Hydrogen production by means of water electrolysis is a potential route to an energy sustainable future [4]. Currently, the efficiency of hydrogen production by water electrolysis is too low to be economically competitive for real energy requirements [5]. Consequently, efficient catalysts are sought to ensure good HER performance. In this regard, noble metals, such as platinum, exhibit the highest electrocatalytic activity, but their shortage and high cost restrict their large-scale application [6]. Therefore, efficient and economical catalysts research is crucial for the development of this technology.

Graphene-based materials

Graphene has attracted extensive attention due to its excellent physical and chemical properties, large surface area, excellent electrical conductivity and high mechanical strength [7]. Pure graphene is catalytically inactive for HER due to its flat and inert surface [8]. Therefore, graphene undergoes different doping, functionalization

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and strain processes with the objective of tune its chemical properties. Fortunately, graphene derivatives such as reduced graphene oxide (rGO) can be synthesized by the simple Hummers method and used as precursor for a wide range of graphene-based materials [9]. Because of residual oxygenated groups and defects, the conductivity of rGO is lower than that of pristine graphene. However, reactive surfaces of GO and rGO enable the optimization of specific properties and ease the incorporation of the dopant or composite.

Doping has been widely investigated in order to specifically tailor the catalytic properties [10]. The creation of charged groups and defects in the graphene network by modifying the carbon atoms surface gives place to defective graphene materials that present an alteration of the geometry and the electronic structure. These materials are used as electrocatalysts since they can induce lower activation barriers or improved adsorption energy to reactants, products or intermediate species, being able to achieve higher catalytic activities or selectivity towards certain reactions [11]. Moreover, it is well known that topological defects or edges are related to the electrocatalytic performance so a large amount of defects can lead to enhance the graphene catalytic activity [12].

Heteroatom-doped metal-free graphene catalysts

Heteroatom-doped noble metal-free catalysts have been synthesized (i.e., nitrogen, sulphur, fluorine, boron, phosphorus, etc.) tuning its electronic properties for enhancing hydrogen evolution reaction. In this regard, nitrogen doping has been an effective way to tune the properties of graphene contributing to its development for various applications. The nitrogen bonding configuration normally obtained are pyridinic N, pyrrolic N, and graphitic N [8]. It has also been reported nitrogen and sulphur co-doping leads to higher activity of graphene in HER at low operating potential (Figure 1) obtaining comparable results to 2D MoS_2, the best Pt-free HER catalyst [7]. Also, nitrogen and phosphorus dual-doped graphene has been studied exhibiting comparable onset overpotential, Tafel slope and exchange current density to some of the traditional metallic catalysts [13,14] due to the synergistic effect of the dopants.

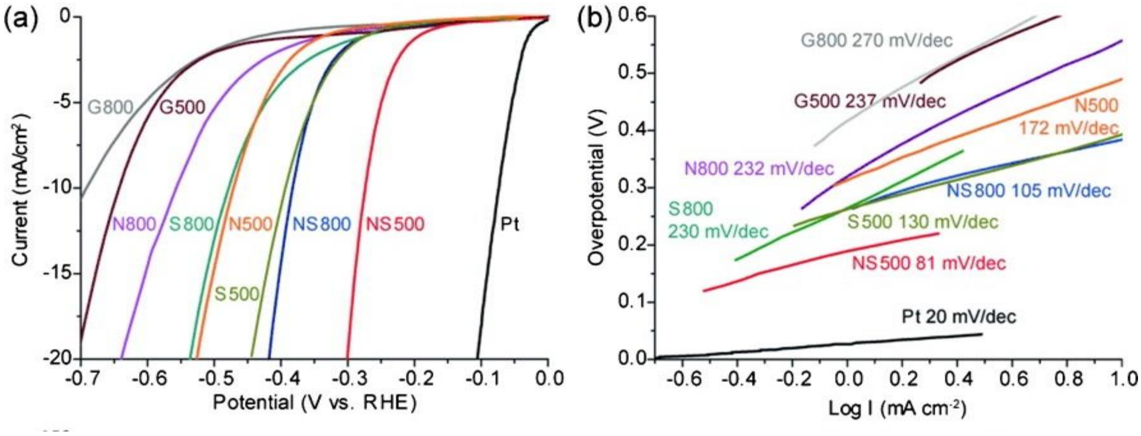

Figure 1. HER activity of chemically doped nanoporous graphenes: G (graphene), N (N-doped graphene), S (S-doped graphene) and NS (NS-doped graphene). a) CV curves of the samples produced at different chemical vapor deposition temperatures and with different dopants in comparison to Pt; b) Tafel plots for the different samples. Reproduced with permission (ref. 7).

Boron has also emerged as doping heteroatom in several technological fields [11,15]. It has been demonstrated that B-substituted graphene synthetized by controlled substitution of the C atoms is an efficient metal-free electrocatalyst for HER [11] and B-doped graphene can lower the conversion barriers for the transformation of H^+ ions to H_2 showing a better HER activity than undoped graphene [16].

Noble metal-free graphene catalysts

The nonprecious transition metal insertion (Mn, Co, Cu, Ni, etc.) has also been investigated obtaining satisfactory results displaying high HER performances due to an active metal-H bond interaction and similar electronic structure to Pt [16,17]. In this field, ultra-small ruthenium phosphide nanoparticles grown on reduced graphene oxide nanosheets were reported has a highly efficient HER catalyst achieving superior current density at extremely low overpotentials than commercial Pt/C [18]. Furthermore, Deng et al. found out increasing the amount of nitrogen doping and reducing the number of graphene layers that encapsulate a CoNi nanoparticle can significantly increase the electron density enhancing the HER activity in acidic media [19]. On the other hand, sulphur-doped graphene has recently attracted as a promising material beyond N-doped graphene displaying to be competitive or even better compared to N-doped materials for ORR activity. Recently it has been investigated as a noble metal-free catalyst for HER in acidic media obtaining a significantly enhance to HER activity of graphene attributed to the presence of high S-doping level with thiophene-S rich species [16]. Figure 2 shows the role of S-doping level, species types/contents, and defect level towards HER in acid media.

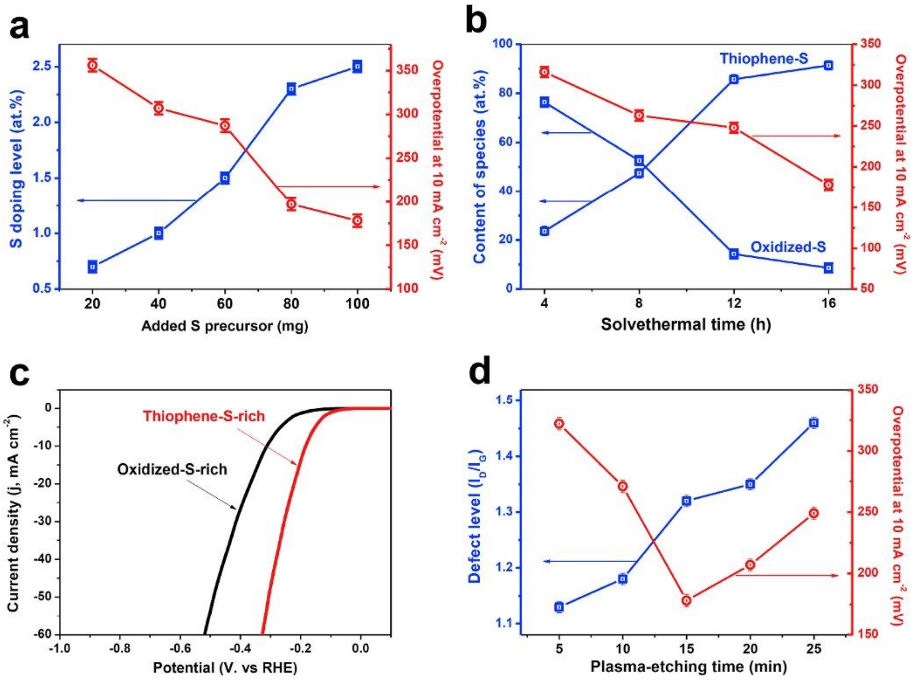

Figure 2. (a) HER activities (overpotential at 10 mA cm^{-2}) of sulphur-doped graphene (SG) samples with different S-doping levels obtained by varying the amount of added S precursor. (b) HER activities of SG samples with different compositions of thiophene-S/oxidized-S species obtained by varying the solvothermal time during the synthesis of SG. (c) Polarization curves of thiophene-S-rich and oxidized-S-rich SG samples in 0.5 M H_2SO_4 solution at a scan rate of 5 mV s^{-1}. (d) HER activities of SG samples with different topological defect levels (I_D/I_G ratio) obtained by varying the plasma-etching time. Reproduced with permission (ref. 16).

In addition, co-doping materials with metal and non-metal pairs with high catalytic performance have also been reported showing dual-doped multilayer graphene exhibit higher HER activity than mono-doped materials as a result of a synergetic dual-doped effect [13]. Regarding this, nitrogen-doped graphene materials are the ones with the highest HER performance [20], especially, Co and Cu embedded N-enriched mesoporous carbon showed high catalytic ability in HER [21]. Besides, recent theoretical studies support the HER performance can be dramatically improved on waved graphene due to localized chemical potential and Pt-analogous activity showing Ni-N and V-N co-doped graphenes have the highest catalytic ability [22]. Graphene-

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encapsulated CoNi and RuCo nanoalloys have been reported to have a high HER activity due to the thin nitrogen-doped graphene layer protecting the alloy from corrosion and simultaneously promoting the electron penetration of the transition metals to the carbon surface [19,23]. A similar synergistic effect has been shown for iron nanoparticles [24].

Graphene-based composite catalysts

Graphenic materials have been used to synthesize different 1D, 2D and 3D nanocomposites with enhanced catalytic activity toward the HER. For instance, 2D nanomaterials composed by MoCoFeS supported on reduced graphene oxide (rGO) showed good electrochemical performance for HER [25]. Additionally, Figure 3 reveals that iron-doped tungsten oxide nanoplate supported on rGO nanocomposite (Fe-WOxP/rGO) exhibited excellent electrocatalytic activity towards HER due to the coupled synergic effect between many oxygen vacancies formation on tungsten oxide in the nanoplate structure of Fe-WOxP and rGO nanosheet [26]. Moreover, monodisperse PdRuNi nanoparticles decorated on graphene oxide were synthesized showing an exceptional performance and stability [27].

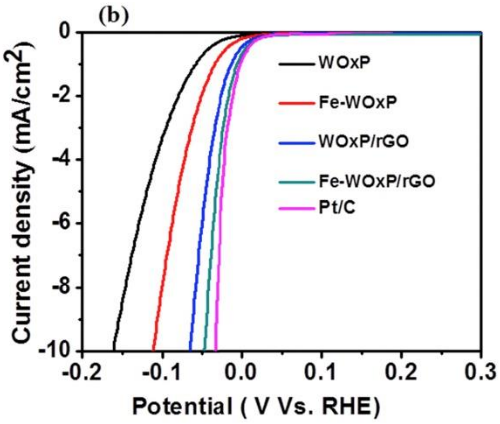

Figure 3. Hydrogen evolution on WOxP, Fe-WOxP, WOx/PrGO, Fe-WOxP/rGO, and Pt/C recorded in 0.5 M H_2SO_4 at 2 mV s^{-1}. Reproduced with permission (ref. 26).

Furthermore, a reduced graphene oxide/metallic MoSe2:Cu nanosheet has been synthesized and shown to be effective, as the Cu doping and the interface effect between MoSe2 and rGO increased the conductivity of the material, resulting in an active and stable catalyst [28].

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Finally, Table 1 reports and compares the main physicochemical properties and catalytic performances towards the HER of non-precious metal graphene catalysts.

Table 1. Physicochemical properties of non-precious metal graphene catalysts.

Catalyst	**Non metal Doping Elements**	**Metal doping elements**	**Onset overpotential (mV vs RHE)**	**Tafel slope (mV·dec^{-1})**	**Ref.**
Ultrathin graphene shells encapsulated in a uniform CoNi nanoalloy	-	Co, Ni	142	107	[12]
Plasma-etching on S-graphene	S	-	178	86	[19]
NS-doped nanoporous graphene (NS-500)	N, S	-	280	80.5	[6]
Nitrogen and phosphorus dual-doped multilayer graphene	N, P	-	120	79	[16]
MoP nanoparticle supported on N, P-codoped reduced graphene oxides	N, P	Mo	115	54	[13]
B-substituted graphene	-	B	~200	~99	[10]
Ni-doped graphene	-	Ni	50	45	[15]
Ultrasmall ruthenium phosphide	-	Ru	13	56	[17]

nanoparticles grown on reduced graphene oxide nanosheets					
Co, N-codoped carbon nanotube (CNT) /graphene heterostructure bifunctional catalyst	N	Co	123	67	[18]
Cu, Co-embedded nitrogen-enriched mesoporous carbon framework	N	Cu, Co	145	80	[20]
MoCoFeS/reduced graphene oxide	S	Mo, Co, Fe	110	50	[22]
Phosphine reduced an iron-doped tungsten oxide nanoplate/reduced graphene oxide nanocomposite	P	Fe, W	55	42	[25]

Summary

Herein the general concepts of electrolysers are discussed, with special attention to graphene-based electrocatalysts. Electrolyser is a crucial technology for the desired hydrogen economy since it has the potential to provide pure hydrogen to fuel cells. With the aim to solve the principal catalytic problems at the cathode electrode of this device, the new advances in non-precious metal graphene materials is provided and a summary of the main catalytic properties are reported in Table 1. Along the manuscript, it was

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described diverse methodologies to modify graphene, and therefore its physicochemical properties, with the aim of tailor the properties for future design and synthesis of innovative and sustainable catalysts towards HER. Thus, the current work may help to improve the fabrication of novel electrodes in order to decrease the cost and to enhance the performance of electrolysers.

Acknowledgments

The Spanish Ministry of Economy and Competitiveness (MINECO) has supported this work under project ENE2017-83976-C2-2-R (co-funded by FEDER). G.G. acknowledges the Viera y Clavijo program (ACIISI & ULL) for financial support.

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