Nickel nanoparticles coated on the exfoliated graphene layer as an efficient and stable catalyst for oxygen reduction and hydrogen evolution in alkaline media

Karim Kakaei and Zahra Ostadi
Department of Physical Chemistry and Nanochemistry, Faculty of Science, University of Maragheh, PO Box 55181-83111, Maragheh, Iran
1 Author to whom any correspondence should be addressed.
E-mail: kakaei@maragheh.ac.ir

Keywords: hydrogen evolution, oxygen reduction, nickel, graphene

Abstract
In this work, we report simultaneous electrochemical exfoliation of graphite powder using SDS, anionic surfactant salts, and cyclic potential to prepare graphene on carbon paper. Then, nickel is electro-reduced into graphene nanosheets on carbon paper and also on the bare carbon paper to use in alkaline media for hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR). Afterward, graphene and Ni-graphene are characterized using scanning electron microscopy, atomic force microscopy (AFM) and electrochemical technique. SEM images show the cauliflower-like structure of Ni in the absence of graphene and nanoparticle shapeless in the presence of smooth graphene. The electrochemical results show an excellent catalytic activity of Ni-graphene/ carbon paper with an overpotential of 90 mV (Versus Ag/AgCl), which is lower than the literature value for Ni in alkaline electrolyte for HER (120 mV dec⁻¹). The effect of graphene support on the electrochemical impedance spectroscopy response, activation energy and HER activity of the samples are investigated carefully. Finally, we prepare a novel gas diffusion electrode by using Ni pasted on carbon paper for the ORR in fuel cells and compared it with standard Pt/C catalysts using linear sweep voltammetry.

1. Introduction

Due to urgent demand for the development of energy storage system, the production of clean and renewable fuel attracts great attentions [1, 2]. Several of these sustainable technologies, such as fuel cells, metal-air batteries and electrolyzers, strongly depend on kinetics pathways of oxygen reduction reaction (ORR) [3] and hydrogen evolution reaction (HER) [4, 5]. In spite of extraordinary efforts, developing catalysts for ORR and HER with high activity at low costs remains a grand challenge.

Molecular hydrogen (H₂), which has the highest gravimetric energy density and non-polluting product, is highly regarded as the promising candidate for the future energy storage [6–8]. There are three main methods for hydrogen production namely coal gasification (chemical), steam reforming of hydrocarbons and electrochemical water electrolysis [9]. Nowadays, hydrogen production from coal gasification and methane reforming leads to CO₂ emissions. But, water electrolysis only produces H₂ and O₂ that are clean products. Although tremendous progress has been achieved, highly efficient electro-catalysts or low overpotential still set hurdles for real applications [7, 10–15]. Besides, the current bottleneck of cathode side resides in the sluggish ORR on fuel cells [3, 16]. Hence, study of stable and efficient electro-catalysts for H₂ evolution from water and oxygen reduction for fuel cells still remain a great challenge.

Up to now, noble metal electrocatalysts such as Pt, Au, Ru and Pd still provide the best performance in water splitting for electrolyzers as well as ORR for cathode side of fuel cells, but extensive utilization are seriously limited by the high cost [11, 17–21]. Thus, developing highly active catalysts for HER and ORR based on large surface area, stability of performance, availability in abundant and low cost metals is important to affordable the hydrogen production and fuel cell industries. In regard to this, great progresses have been achieved under the
development of high-performance HER and ORR, excellent durability, cheaper and abundant electro-catalysts such as metal free electrocatalysts [22, 23], transition-metals based hybrid [24], phosphide [25], oxide [26], sulfide [27–29] and carbon-based compounds [30–34].

To date, carbonaceous materials in presence or absence transition–metal nanoparticles have been investigated as novel electro-catalysts for ORR [22, 23, 35], oxygen evolution reaction (OER) [27, 36], methanol oxidation reaction [37], photocatalyst [38, 39] HER [30, 40, 41].

Graphene, 2D form of carbon, has received great scientific attention in recent years due to its high electronic and thermal conductivity, extraordinary of charge mobility, high conductivity, large surface area, etc. [22, 42, 43].

3d transition metals encapsulation into graphene support has been suggested by several researchers as a strategy for HER and ORR in alkaline media [29, 44–47]. Toward this end, Li et al. [30] synthesized the transition metal (Co and Ni) on a graphene protected Ni substrate by a simple electro-deposition method. They found that the Ni/G substrate is stable in alkaline electrolytes and thus can be used as HER catalyst. Moreover, Chang et al [40], found that rGO hybrids with NiCoP could exhibit a comparable HER performance in the alkaline and acidic environment. Recently, interesting finding on the effect of embedded graphene in Fe–Ni electrodes was used for hydrogen generation in alkaline solution [48]. The rGO introduction to porous 3D projections of nanosized Fe–Ni alloy successfully increases the electrochemically active surface area, resulting further water splitting. McKone et al [49], synthesized unsupported Ni–Mo nanopowders that exhibit high catalytic activity for the HER. They evaluated the composition, morphology, catalytic activity, and stability of Ni–Mo nanopowders during hydrogen evolution in aqueous acidic and alkaline conditions in detail. In regard to ORR several groups of researchers have conducted detailed case study of graphene or graphene decorated metal particles. For example, porous nitrogen-doped graphene prepared through pyrolysis of ammonium acetate as an efficient electro-catalyst for ORR. [50]. Jiang et al. [51] prepared a 3D porous cellular NiCoO2/graphene using a sodium dodecyl sulfate via purification assembly of NiCoO2 precursor and rGO for ORR. They reported that the fabricated catalyst shows excellent potentials toward several applications such as metal-air batteries, fuel cells, and water splitting.

But, to the best of our knowledge after extensive literature survey, Ni electrodeposited on graphene electro-synthesis has been unexplored either in synthesis method or for HER and ORR as dual applications. Therefore, this Ni-graphene material is expected to have remarkable potential as electrode material for water splitting and ORR. Other word, the graphene is readily fabricated onto substrate carbon paper by CV in graphite powder and SDS solution and Ni nanoparticles onto graphene substrate. The morphology, catalytic activity, and stability during hydrogen evolution of such catalyst under aqueous alkaline condition have been evaluated in detail.

2. Experimental section

2.1. Graphene synthesis

The graphene nanosheets are synthesized from sodium dodecyl sulfate (SDS) (14 mM), (Fluka), graphite powder (5 mg ml−1), and water with magnetic stirring on carbon paper by in situ cyclic voltammetry (CV) method [52, 53]. The CV was carried out at 50 mV s−1 and 150 cycles in a potential range from 0.22 to −1.7 V at 50 °C and saturated with N2.

2.2. Ni-graphene and Ni-carbon paper electrodes fabrication and Pt/C catalyst

Ni particles were synthesized by electro deposition method on the surface of Carbon paper (b) or graphene coated on carbon paper (c) electrodes from 6 mM NiSO4 and SDS (32 mM) solution with chronoamperometry at 0.25 V relative to Ag/AgCl for 600 s. The Ni loadings on Ni-graphene and Ni-Carbon paper were estimated from the charge consumed during the sweep provided (assuming a 100% current efficiency). In order to compare the fabricated catalysts with standard catalyst we made a mixture containing a homogeneous suspension of commercially available Pt catalyst powder (10 wt%) on carbon black (Vulcan XC-72) E-TEC Inc. as a reference electrocatalyst. Water, Isopropanol (Merck), 10 wt% Nafion solution and Pt based carbon were sonicated for 20 min, then pasted onto carbon paper (TGPH-0120T Toray). The obtained composite was dried in air at 90 °C for 2 h and named Pt/C electrode.

2.3. Electrochemical characterization and measurements

The electrochemical measurements were carried out by a Biologic potentiostat-galvanostat VSP300. A three-electrode cell was applied in all experiments with reference electrode (Ag/AgCl, KCl, 3 M) and Pt as a counter electrode, and carbon paper with or without graphene decorated Ni nanostructure as working electrode in 1M KOH solution for HER and also in 0.1M KOH and saturated O2 for ORR.
3. Results and discussion

The production of graphene was carried out by cyclic voltammetry (CV) technique. Figure 1 shows CV profile of graphene synthesized on carbon paper at potential range from 0 to −1.4 V in colloidal dispersion of 0.10 g graphite with 20 ml SDS (14 mM) in different cycles. This figure 1 shows a broad reduction peak due to the surface oxygen functional groups and reduction of water to hydrogen at −1.25 V [52]. As mentioned in previous works by magnetic stirring of the solution driving graphite onto the electrode surface has occurred [53].

Figure 2 shows the potentiostatic curve, the plot of current versus time, of Ni based carbon paper (b) and Ni deposited on graphene-carbon paper (c). From this figure 2, it can be demonstrated that in the duration time, the currents value decreased dramatically. Moreover, the charge consuming for (b) electrode is much higher than that for (c) electrode, due to the graphene moderately smooth surface than only porous carbon paper as detected in SEM image.

Figure 3 shows the SEM images of graphene on carbon paper. FE-SEM analysis of figures 3(a), (b), and (c) revealed the large, transparent sheets with small layered of graphene planes, growing on a surface of carbon paper. The surface of the aggregated sheets is properly smooth, transparent, and displayed in 3 enlarge with high resolution magnification (1 μm, 500nm and 200nm) to make sure graphene nanosheets is fabricated (i, ii and iii).

In order to directly confirm and identify the thickness and roughness of graphene layers AFM has been applied. The definitive show that the thin flakes in the sample gained by our system a few layers thick is obtained with the AFM.
Figure 3. (a)–(c) FE-SEM micrographs of the surface of graphene on carbon paper with different enlarges.

Figure 4. AFM images of graphene on carbon paper. (i) AFM image and (ii) the height profile of the image.
Figure 4(i) shows the existence of irregularly molded sheets with non-uniform thickness. Figure 4(ii) reveals the height profile obtained along the figure 4(i). The measured thickness of the graphene layers is 1.2–1.5 nm, which is larger than the interlayer spacing of graphite (0.34 nm), reflecting 4–5 nm for graphene layers.

Figures 5(a), (b) reveals a typical FE-SEM micrograph of a cleaned Ni/ carbon paper electrode; the bright shape in figures 5(a), (b) is Ni. As shown in this figure, Cauliflower structure is detected on carbon paper. The average Ni cluster diameter is approximately 100 nm, which is significantly larger than preferred. Figures 5(c),
(d) shows FE-SEM micrograph of amorphous Ni nanoparticles on the 2-dimensional graphene sheets linked carbon paper. By contrast, deposition of several Ni particles on the graphene sheets in the condition like as Ni/carbon paper indicates a much rougher surface and spread amount of Ni nanoparticles. TEM image for Ni nanoparticles decorated on graphene sheets is presented in figure 5(E). This figure displays the spherical shape of the nickel nanoparticles on graphene layers. The average particle size of the nickel nanoparticles was calculated at around 17 nm.

Figure 6 compares the CV curve of the Ni-carbon paper (b) and Ni-graphene carbon paper (c) electrodes in 1 M KOH solution. Polarization was started by scanning potential of 50 mV s$^{-1}$ from 0.6 V to −0.2 V versus Ag/AgCl. This figure displays the redox peaks for Ni-carbon paper(b) in the positive potential side (272 and 342 mV), this pair of peaks is related to the oxidation of Ni(OH)2 to NiOOH [54]. Also figure 6 shows the CV profile of Ni-graphene carbon paper (c) which Ni nanoparticle is deposited on the graphene based carbon paper. The potential peak of (c) electrode in forward and backward scan of CV curve has been shifted to the positive voltage which can be attributed to the influence of the graphene on the Ni deposition. Moreover, the higher Ni content in (b) electrode in comparison to (c) electrode will lead to increase the intensities of the redox activation peaks in (b).

The electrocatalytic HER performance of the electrocatalyst nanostructures were investigated in basic aqueous solution (1 M KOH) by linear sweep voltammetry (LSV). The LSV curves of the bare carbon paper (a), Ni-carbon paper (b), Ni-graphene carbon paper (c) and commercial Pt/C catalyst at a scan rate of 1 mV s$^{-1}$ are seen in figure 7. As predictable, the Pt/C (d) electro-catalyst, selected as reference, shows the highest HER catalytic activity with 35 mV overpotential. However, the bare carbon paper (a) exhibits very poor HER activity with approximately 350 mV overpotential (figures 7(i) and (ii)). In addition, the (c) electrode exhibits lower overpotential than (b) electrode. On the other hand, an interesting trend for HER performance could be observed as following: (d > c > b > a). Furthermore, the difference in performance between (b) and (c) was probably resulted from the difference in presence of graphene as a support for Ni nanoparticle that is Caulifower structure or irregular solid shapes with nanosize, reflecting the significance of graphene sheets.

Moreover, the Tafel plots of different electrodes are shown in figure 7(iii). The Tafel slope of Pt/C catalyst (d) as a control electrode is about 70 mV dec$^{-1}$, lower than all other catalysts (c) 95 mV dec$^{-1}$ and (b) 130 mV dec$^{-1}$. The reported Tafel slope in literature for Ni in alkaline electrolyte is nearly 120 mV dec$^{-1}$. Thus, reducing the Tafel slope to around 95 mV dec$^{-1}$ for Ni-graphene carbon paper is the remarkable electrocatalytic HER property of graphene which might be resulted from faster electron transfer. LSV Polarization for Ni–graphene/ carbon paper before and after continuous LSV scanning of 1000 cycles is shown in figure 7(iv).

We further studied the effect of electrolyte temperature on the catalytic activity at the designed electrocatalyst (c electrode) for HER. Figure 7(v) shows the LSV polarization curves of the Ni deposited on graphene-carbon paper (c) at different temperatures. With increasing the temperature from 298 to 323 K, the HER overpotential decreased from value about 90 mV to 60 mV and the current density enhanced with the rise of temperature. The obtained results from LSV curves indicate that the current density can be significantly enhanced by increasing the electrolytic temperature, demonstrating the higher electrocatalytic activity and lower ohmic resistance of the cell. Figure 7(vi) shows the Arrhenius curve, the plot of the logarithm of the current density ln($i_0$) versus the inverse temperature (1/T) [55], for the water splitting of the synthesis Ni–graphene/ carbon paper(c) as a best electrode in this work. The exchange current densities ($i_0$) were obtained by applying...
the extrapolation method to the Tafel plots (figure 7(v)). The calculated value of $E_a$ was 56.66 kJ mol$^{-1}$ for HER, suggesting the higher HER activity.

The measured activation energy for the (c) catalyst was lower than that of the Ni$_2$P/RGO hybrid catalyst, which yields an activation energy of 63 kJ mol$^{-1}$ [56].

The catalytic durability was another key important parameter for HER performance. To obtain their long term stability, the catalysts were tested at high overpotential ($\eta = 260$ mV) to evaluate the I-t curves. As shown in figure 8(i) the (c) electrode with graphene demonstrated excellent stability. Remarkably, there was minor current loss at the beginning I-t curve. The sample without graphene (b) exhibited poor stability. As a control, the current density of Pt/C decreased slowly (d).
Figure 8. (i) The time dependence of current density of (b), (c) and commercial Pt/C(d) at a overpotential of 260 mV for 7000 s (ii) Nyquist plots measured under an overpotential of 200 mV from 100 kHz to 100 mHz.

Figure 9. RDE voltammograms recorded in O₂ saturated 0.1 M KOH with different RPM (i) Ni-graphene on GCE, (ii) Pt/C on GC. (iii) Koutecky–Levich plots of J⁻¹ versus ω⁻¹/₂ at different potential for Ni-graphene obtained from the LSV curves in (i). (iv) Koutecky–Levich plots of J⁻¹ versus ω⁻¹/₂ at different potential for Pt/C obtained from the LSV curves in (ii) and (v) Polarization curves of Pt/C, Ni-graphene and Ni on carbon paper as gas diffusion electrodes for ORR in 0.1 M KOH, at ambient temperature.
The a.c. impedance investigation of the HER on the electrodes for the samples was achieved at selected overpotentials (\(\eta = 200 \text{ mV}\)) in 1 M KOH to better understand the underlying origin. The obtained plots are presented in figure 8(ii). It should be noticed that there is no any Warburg impedance for all samples, which illustrates the fast ionic transport and kinetic control of the electrolysis reaction on the surface of the electrodes predominant [57]. As shown from figure 8(ii) the Nyquist diagram of the electrodes shows only one semicircle at the complex plane. It could be seen that the value of charge transfer resistance for Pt/C(d) was smaller than that for (c) and (c) electrode is much smaller than those for (b) and (a) at the same overpotential, in well agreement with their different HER activities.

To evaluate the ORR electrocatalytic performance of the Ni-graphene catalyst, rotating disk electrode (RDE) measurements were employed in alkaline electrolyte (0.1 M KOH) at several rotation speeds. Ideal ORR catalysts should electrocatalyze ORR via a four-electron pathway rather than in an indirect two-electron process. Figure 9(i) and iii shows linear LSVs of Ni-graphene and Pt/C catalysts on GC with RDE in O\(_2\)-saturated KOH electrolyte at several rpm. As shown in this figure the diffusion-limiting current density of Ni-graphene is higher than that of the commercial Pt/C, demonstrating its distinct electrocatalytic activity for ORR.

Moreover, the limiting current densities observed on modified GC electrodes increases gradually as the rotation speed increases. This tendency proposes that the diffusion of O\(_2\) increase at the surface of the Ni-graphene and Pt/C electrodes. Figures 9(ii) and (iv) displays the Koutecky-Levich (K–L) plots of Ni-graphene and Pt/C catalysts respectively. This figure represents the relationship between the inverse current density (\(j^{-1}\)) and the inverse square of the root of the rotation rate (\(\omega^{-1/2}\)) at various voltages. Furthermore, the near parallelism of the fitting plots suggests a similar electron transfer number (n) for both electrodes (n = 3.91 for Ni-graphene and n = 3.98 for Pt/C). Figure 9(v) shows the LSV measurements at the different gas diffusion electrodes (geometric area of 1 cm\(^2\)) for the Ni/carbon paper, Ni-graphene/carbon paper and Pt/C on carbon paper in O\(_2\)-saturated 0.1 M KOH at a scan rate of 5 mV s\(^{-1}\). The obtain kinetic parameters of the electrodes in low current density reign were calculated to be 85, 71 and 53 mV dec\(^{-1}\) for Ni/graphene, Pt/C on carbon paper and Ni-graphene/carbon paper, respectively.

4. Conclusions

In this work, graphene nanosheets are prepared using graphite powder in SDS surfactant by CV, as green and eco-friendly, method. Graphene is successfully characterized by employing FE-SEM and AFM techniques. FE-SEM results confirm the graphene films on the surfaces of the carbon paper are quite thin and smooth. We also employed CV to deposit Ni on graphene surface to use as water splitting. SEM micrographs for Ni nanoparticle on carbon paper and graphene surfaces show Cauliflower structure for Ni on carbon paper and shapeless with higher dispersion on graphene between 60 and 40 nm diameters. The prepared electrodes were characterized using different electrochemical techniques for use as an active and stable catalyst for the HER and ORR in alkaline solution. It was found that the Ni-graphene based carbon paper has a superior activity in the HER than that Ni based only carbon paper. For example, low Tafel slope, low overpotential, values and high stability of Ni/graphene paper confirmed the low consumption of energy during the electrolysis of water. Moreover, K–L plot illustrates that 4-electron participates in the alkaline solution for ORR. The presence of graphene as a support hinders the nickel Cauliflower structure growth, leading to decreasing Ni nanoparticle size, which can increase the catalytic activity.

ORCID iDs

Karim Kakaei https://orcid.org/0000-0001-6820-696X

References

[1] Kakaei K, Hamidi M and Kakaei N 2019 Simultaneous electro-synthesis of polyaniline graphene nanocomposite in dilute graphene oxide as dopant and aniline by electrochemical method and its high specific capacitance Mater. Res. Express 6 085623
[2] Kakaei K and Ghadimi G 2020 A green method for Nitrogen-doped graphene and its application for oxygen reduction reaction in alkaline media Mater. Technol. 1–8
[3] Zhiani M, Gharibi H and Kakaei K 2010 Optimization of Nafion content in Nafion–polyaniline nano-composite modified cathodes for PEMFC application Int. J. Hydrogen Energy 35 9261–8
[4] Askari M B, Salarizadeh P, Rozati S M and Seiﬁ M 2019 Two-dimensional transition metal chalcogenide composite/reduced graphene oxide hybrid materials for hydrogen evolution application Polyhedron 162 201–6
[5] Singh C and Das S K 2019 Anderson polynoxometalate supported Cu(II)@phen complex as an electrocatalyst for hydrogen evolution reaction in neutral medium Polyhedron 172 80–6
[6] Zhuang M et al 2016 Polymer-embedded fabrication of Co2P nanoparticles encapsulated in N,P-doped graphene for hydrogen generation Nano Lett. 16 6691–8
[7] Zhou W et al 2016 Recent developments of carbon-based electrocatalysts for hydrogen evolution reaction Nano Energy. 28 29–43
[8] Barakat N A M, Ahmed E, Amen M T, Abdelkareem M A and Farghali A A 2018 N-doped Ni/C/TiO₂ nanocomposite as effective photocatalyst for water splitting Mater. Lett. 210 (Suppl C) 317–20

[9] Huang Y-G et al 2016 The effect of graphene for the hydrogen evolution reaction in alkaline medium Int. J. Hydrogen Energy 41 3786–93

[10] Zhang X, Xu H, Li X, Li Y, Yang T and Liang Y 2016 Facile synthesis of nickel–iron/nanocarbon hybrids as advanced electrocatalysts for efficient water splitting ACS Catal. 6 580–8

[11] Zhang M, Wang S, Li T, Chen J, Zhu H and Du M 2016 Nitrogen and gold nanoparticles co-doped carbon nanofiber hierarchical structures for efficient hydrogen evolution reactions Electrochim. Acta 208 1–9

[12] Yan X et al 2016 From water oxidation to reduction: transformation from NiCo₃₋ₓOₓ Nanowires to NiCo/NiCoOx Heterostructures ACS Applied Materials & Interfaces 8 3208–14

[13] Xu, X., Nosheen F and Wang X 2016 Ni-decorated molybdenum carbide hollow structure derived from carbon-coated metal–organic framework for electrocatalytic hydrogen evolution reaction Chem. Mater. 28 6313–20

[14] Xing C et al 2016 Structural evolution of co-based metal organic frameworks in pyrolysis for synthesis of core–shell nanosheets: Co₉Co₆Oₓ@Carbon–rGO composites for enhanced hydrogen generation activity ACS Applied Materials & Interfaces. 8 15430–8

[15] Wang A-L, Xu H and Li G-R 2016 NiCo layer triple doped hexisides with porous structures as high-performance electrocatalysts for overall water splitting J. Electrochem. Energy Lett. 1 445–53

[16] Liu L, Zeng G, Chen J, Bi L, Da L and Wen Z 2018 N-doped porous carbon nanosheets as pH-universal ORR electrocatalyst in various fuel cell devices Nano Energy. 49 393–402

[17] Khanova L A and Krishilik L 2011 Kinetics of the hydrogen evolution reaction on gold electrode. A new case of the barrierless discharge J. Electroanal. Chem. 660 224–9

[18] Quaino P and Santos E 2015 Hydrogen evolution reaction on palladium multilayers deposited on Au(111): a theoretical approach Langmuir 31 858–67

[19] Naga Mahesh K, Balaji R and Dhatathreyan K S 2016 Palladium nanoparticles as hydrogen evolution reaction (HER) electrocatalyst in electrochemical methanol reformer Int. J. Hydrogen Energy 41 1645–52

[20] Heider E A, Jacob T and Kibler L A 2018 Platinum overlayers on PtSui–x(i11) electrodes: tailoring the ORR activity by lateral strain and ligand effects J. Electroanal. Chem. 819 289–95

[21] Tavakoli M et al 2017 Electrochemical activation of single-walled carbon nanotubes with pseudo–atomic-scale platinum for the hydrogen evolution reaction in gas diffusion electrode J. Electrochemical Science 7 3121–30

[22] Kakaei K and Balavandi A 2017 Hierarchically porous fluorine–doped graphene nanosheets as efficient metal-free electrocatalyst for oxygen evolution in gas diffusion electrode J. Colloid Interface Sci. 490 819–24

[23] Kakaei K and Balavandi A 2016 Synthesis of halogen-doped reduced graphene nanosheets as efficiently metal-free electrocatalyst for oxygen reduction reaction J. Colloid Interface Sci. 463 46–56

[24] Kakaei K, Esrafili M D and Ehsani A 2019 Chapter 5 - graphene-based metal particles, ed K. Kakaei, M D Esrafili and A Ehsani (Interface Science and Technology: Elsevier) pp 153–202

[25] Li Y, Zhang H, Jiang M, Kuang Y, Sun X and Duan X 2016 Ternary NiCoP nanosheet arrays: an excellent bifunctional catalyst for alkaline overall water splitting Nano Res 9 2251–9

[26] Xu Y-F, Gao M-R, Zheng Y-R, Jiang J and Yu S 2013 Nickel/Nickel(II) oxide nanorods anchored onto cobalt(IV) diselenide nanobelts for the electrochemical production of hydrogen Angew. Chem. Int. Ed. 52 8546–50

[27] Ouyang C et al 2015 Hierarchically Porous NiSₓ nanorod array foam as highly efficient electrocatalyst for hydrogen evolution reaction and oxygen evolution reaction Electrochim. Acta 174 297–301

[28] Fang W, Liu D, Liu Q, Sun X and Asiri A M 2016 Nickel promoted cobalt disulphide nanowire array supported on carbon cloth: an efficient and stable bifunctional electrocatalyst for full water splitting Electrochem. Commun. 63 60–4

[29] Sumboja A et al 2019 Sulfur-rich colloidal nickel sulfides as bifunctional catalyst for all-solid-state, flexible and rechargeable zinc-air batteries ChemCatChem 11 1205–13

[30] Li X, Zhang L, Huang M, Wang S, Li X and Zhu H 2016 Cobalt and nickel selenide nanowalls anchored on graphene as bifunctional electrocatalysts for overall water splitting Journal of Materials Chemistry A 4 14789–95

[31] Krishna R, Fernandes D M, Dias C, Ventura J, Freire C and Titus E 2016 Facile synthesis of novel Co-Bi/Ni/RGO nanocomposite as a cost effective catalyst for improved hydrogen generation with enhanced electrochemical activity Int. J. Hydrogen Energy. 41 11498–509

[32] Zheng Y et al 2014 Hydrogen evolution by a metal-free electrocatalyst Nat. Commun. 5 3783

[33] Duan J, Chen S, Jaroniec M and Qiao S Z 2015 Porous Cu₃Nₓ Nanolayers®N-graphene films as catalyst electrodes for highly efficient hydrogen evolution ACS Nano. 9 931–40

[34] Thi M T N, Tran T H, Hai Anh P D, Nhac-Vu H T and Bui Q B 2019 Hierarchical zinc–nickel phosphides nanosheets on 3D nickel foam as self-support electrocatalysts for hydrogen evolution reaction Polyhedron 168 80–7

[35] Kakaei K, Javan H, Khamfroush M and Zarei S A 2016 Fabrication of new gas diffusion electrode based on carbon quantum dot and its application for oxygen reduction reaction J. Electrochem. Soc. 164 41604–91

[36] Tahir M et al 2015 Bifunctional catalysts of Co₉O₈@GCN tubular nanostructured (TNS) hybrids for oxygen and hydrogen evolution reactions Nano Research. 8 3725–36

[37] Kakaei K, Javan H and Mohammadzadeh H B 2016 Synthesis of carbon quantum dots nanoparticles by cyclic voltammetry and its application as methanol tolerant oxygen reduction reaction electrocatalyst J. Chem. Chin. Soc. 63 432–37

[38] Wei J, Wang Z, Zhang Y, Wang M, Du J and Tang X 2017 Enhanced performance of light-controlled switching in hybrid cuprous oxide/reduced graphene oxide (Cu₂O/rGO) nanocomposites Opt. Lett. 42 911–4

[39] Zhang Z, Zeng X, Wang M, Hu W, Liu C and Tang X 2017 Tunable photoluminescence of water-soluble AgInZnS–graphene oxide (GO) nanocomposites and their application in vivo bioimaging Sensors Actuators B 252 (Supplement C) 1179–86

[40] Li et al 2016 Mechanistic Insights on Ternary Ni₂–xCo₃P for hydrogen evolution and their hybrids with graphene as highly efficient and robust catalysts for overall water splitting Adv. Funct. Mater. 26 6783–96

[41] Subramanya B, Ullal Y, Shenoy U S, Bhat D K and Hegde A C 2015 Novel Co–Ni–graphene composite electrodes for hydrogen production RSC Adv. 5 47398–407

[42] Kakaei K and Marzang K 2016 One-step synthesis of nitrogen doped reduced graphene oxide with NiCo nanocomposites for hydrogen generation and their application in alkaline medium J. Colloid Interface Sci. 462 148–53

[43] Kakaei K, Rahimi A, Huseinidost S, Hamidi M, Javan H and Balavandi A 2016 Fabrication of Pt–CeO₂ nanoparticles supported sulfonated reduced graphene oxide as an efficient electrocatalyst for ethanol oxidation Int. J. Hydrogen Energy 41 3861–9

[44] Jazini L et al 2017 Synthesis of 3D-MoO₃ microsphere supported MoS₂ as an efficient electrocatalyst for hydrogen evolution reaction Nanotechnology 28 465504
[45] Dawei Z et al 2018 Ni$_3$S$_2$ nanowires grown on nickel foam as an efficient bifunctional electrocatalyst for water splitting with greatly practical prospects Nanotechnology 29 245402
[46] Jang D et al 2017 Ni-O$_4$ species anchored on N-doped graphene-based materials as molecular entities and electrocatalytic performances for oxygen reduction reaction Solid State Sci. 74 56–61
[47] Carrillo-Rodriguez J C et al 2017 Easy synthesis of N-doped graphene by milling exfoliation with electrocatalytic activity towards the Oxygen Reduction Reaction (ORR) Int. J. Hydrogen Energy 42 30383–8
[48] Badrasyana S, Bhat D K, Shenoy S, Ullal Y and Hegde A C 2015 Novel Fe–Ni–Graphene composite electrode for hydrogen production Int. J. Hydrogen Energy 40 10453–62
[49] McKone J R, Saddler B F, Werlang C A, Lewis N S and Gray H B 2013 Ni–Mo Nanopowders for efficient electrochemical hydrogen evolution ACS Catalysis. 3 166–9
[50] Hassani S S, Samiee L, Ghasemy E, Rashidi A, Ganjali M R and Tasharrofi S 2018 Porous nitrogen-doped graphene prepared through pyrolysis of ammonium acetate as an efficient ORR nanocatalyst Int. J. Hydrogen Energy 43 15941–51
[51] Jiang S, Ithisuphalap K, Zeng X, Wu G and Yang H 2018 3D porous cellular NiCoO$_2$/graphene network as a durable bifunctional electrocatalyst for oxygen evolution and reduction reactions J. Power Sources 399 66–75
[52] Kakaei K 2013 One-pot electrochemical synthesis of graphene by the exfoliation of graphite powder in sodium dodecyl sulfate and its decoration with platinum nanoparticles Carbon 51 195–201
[53] Kakaei K and Gharibi H 2014 Palladium nanoparticle catalysts synthesis on graphene in sodium dodecyl sulfate for oxygen reduction reaction Energy 65 166–71
[54] Barakat N A M, Motlak M, Elzatahry A A, Khalil K A and Abdelghani E A M 2014 Ni$_x$Co$_{1−x}$ alloy nanoparticle-doped carbon nanofibers as effective non-precious catalyst for ethanol oxidation Int. J. Hydrogen Energy 39 305–16
[55] Gharibi H, Kakaei K, Zhiani M and Taghiabadi M M 2011 Effect of polyaminol-doped trifluoromethane sulfonic acid nanofiber composite film thickness on electrode for methanol oxidation Int. J. Hydrogen Energy 36 13301–9
[56] Pan Y et al 2015 Nickel phosphide nanoparticles-nitrogen-doped graphene hybrid as an efficient catalyst for enhanced hydrogen evolution activity J. Power Sources 297 65–52
[57] Kakaei K, Ebrahimi M D and Ehsani A 2019 Chapter 7 - alcohol oxidation and hydrogen evolution ed K Kakaei, M D Ebrahimi and A Ehsani (Interface Science and Technology: Elsevier) pp 253–301