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Ni/NiO@rGO as an efficient bifunctional electrocatalyst for enhanced overall water splitting reactions

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Highlights

- Ni/NiO@rGO hierarchical nanostructures were synthesized by chemical synthesis method.
- Morphological tuning was successfully correlated with synthesis parameters.
- Ni/NiO@rGO had highest electrocatalytic activity for overall water splitting reactions.
- Oxygen containing sites of GO and of Ni/NiO NPs were less catalytic than Ni/NiO@rGO.
- Ni/NiO NPs decoration on GO leading to simultaneous enhancement of stability and activity from their cooperation.

Abstract

Herein, we fabricated bifunctional, noble metal-free, highly efficient nickel/nickel oxide on reduced graphene oxide (Ni/NiO@rGO) by chemical synthesis approach for electrochemical water splitting reaction. Its structural and morphological characterization using thermogravimetric analysis (TGA), transmission electron microscopy (TEM), field emission scanning electron microscope (FESEM), energy dispersive analysis of X-ray (EDAX) and X-ray diffraction (XRD) represents, Ni/NiO@rGO is having Ni/NiO NPs ~10 nm (±2 nm) on graphene oxide with face-centered cubic (FCC) crystal structure. Moreover, the presence of Ni/NiO (2.26%), O (6.56%), N (0.74%) and C (90.44%) from EDAX analysis further confirms the formation of Ni/NiO@rGO and it also supported by FTIR studies. This nanocatalyst is examined further for electrocatalytic water splitting reactions (HER and OER). It demonstrated low overpotential 582 mV to achieve current density at 10 mAcm^{-2} and smaller Tafel slope of 63 mV dec^{-1} obtained in 0.5 M H_2SO_4 towards HER. Also, at the other end at onset potential of 1.6 V vs. RHE towards OER. It demonstrated low overpotential 480 mV to achieve current density at 10 mAcm^{-2} and smaller Tafel slope of 41 mV dec^{-1} in 0.5 M KOH towards OER observed. Hydrogen fuel is eco-friendly to the environment and noteworthy performance of earth-saving reactions.

Introduction

Energy and anxiety environmental issues have fetching very critical issue day by day, mainly due to over combustion of fossil fuels. Hence, its urgent need to specifically design its alternative way for the development of clean, quiet and more efficient energy resources such as hydrogen fuel (zero carbon emission fuel when burned with oxygen) [1]. Hydrogen energy is a consumable energy source for fossil fuel in the near future and recyclable to the environment. Hydrogen is the most abundant element with a variety of molecular forms such as H_2O, coal, and others but other side of the fact is H_2 gas does not exist on earth naturally. There is an economic demand to develop an easier and cleaner path for production of H_2 because of is having high energy efficiency equivalent to the electrical energy [2].

Therefore, precious metals such as Pt, Ag, Au, Pd, Ir, Rh and Ru are more stable catalyst commonly used in water splitting reactions. Pt-based nano-electrocatalyst which applicable to the hydrogen evolution reaction (HER) and Ru and Ir are more favourable for oxygen evolution reaction (OER) [3]. But their expensive and rare availability in nature limits its utilization [4], [5]. Replacing these noble metal catalyst with earth abundant and cost-effective systems it becoming a challenge of ongoing research in the line with hydrogen energy [6], [7]. Moreover, minimize the use of electrocatalytic system

followed by increase its performance by controlling their size at nano-regime is also one of the challenge. In view of this on-going development of cheaper and more active, nano-based bifunctional (both for HER and OER) electrocatalysts will probably decrease the gap between precious-nonprecious followed by its promotion towards commercialization.

A large number of efficient electrocatalysts such as earth-abundant metals, alloys, sulfides, carbides, and metal-carbon nanocomposite has proposed for overall water splitting reactions. For example, Cu_2ZnSnS_4 [8], Ni_3Se_2 [9], $Fe_{10}Co_{40}Ni_{40}P$ [10], Ni_2CoP [11], $NiSe_2$ [12], carbon nanotubes (CNTs), C_{60}, graphene oxide (GO) and other carbon allotropes, heteroatom-doped carbon nanomaterials and metal oxide modified carbon nanomaterials are also outstanding electron carriers [13]. On the basis of these electrocatalysts, we have synthesized novel bifunctional carbon-metal framework electrocatalysts for overall water splitting reactions (HER and OER) [14], [15], [16] and schematically shown in Scheme 1.

Herein, scalable synthesis of low cost, exceedingly and similarly active like Pt electrocatalyst, in the electrochemical tests demonstrated that the Ni/NiO@rGO nanocomposite exhibit excellent catalytic activity and high selectivity toward OER and HER. To the best knowledge, this is the first report of a low cost, highly stable and active Ni/NiO@rGO based bifunctional (anode and cathode) material.

Section snippets

Chemicals

Graphite powder (extra pure), sulphuric acid (98%, H_2SO_4), nitric acid (78%, HNO_3), acetone, alcohol, nickel (II) acetate tetrahydrate, ethylene glycol (EG), isopropanol and nafion all chemicals are of analytical grade and were purchased from s. d. fine, India. Double distilled water (DDW) used for all synthesis and de-ionized water for electrochemical studies.…

Synthesis of reduced graphene oxide (rGO)

For the synthesis of rGO, initially 100 mg of graphite powder was taken in a mixture H_2SO_4 98% and HNO_3 78% in the ratio of 3:1…

Results and discussion

The sheet like structure of functionalized rGO can be undoubtedly known from Fig.3(a). The morphology of the products obtained by the modified Hummers' method.[22b] Fig.3(b) represented the Ni/NiO@rGO nanocomposite material and Ni/NiO NPs are found to be randomly distributed on the rGO sheets. Moreover, it is also clearly visible Ni/NiO NPs decoration on the rGO sheet at low percentage. Ni/NiO NPs percentage shows in the Fig.3(c). EDS spectra and other elements like C, N and O and Ni as…

Conclusion

Herein, we synthesized Ni/NiO@rGO composite material as bifunctional electrocatalytic material for overall water splitting reaction. These materials show bifunctional electrocatalytic activities is better than their counter materials like Ni/NiO and rGO could be due to their cooperative interactions. Interestingly, Ni/NiO@rGO composite shows HER onset at −0.4V vs RHE as well as OER at 1.6V vs RHE in acidic and basic medium respectively. Moreover, its Chronoamperometric current stability is…

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