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# Cobalt and Nickel ferrites based Graphene Nanocomposites for Electrochemical hydrogen evolution

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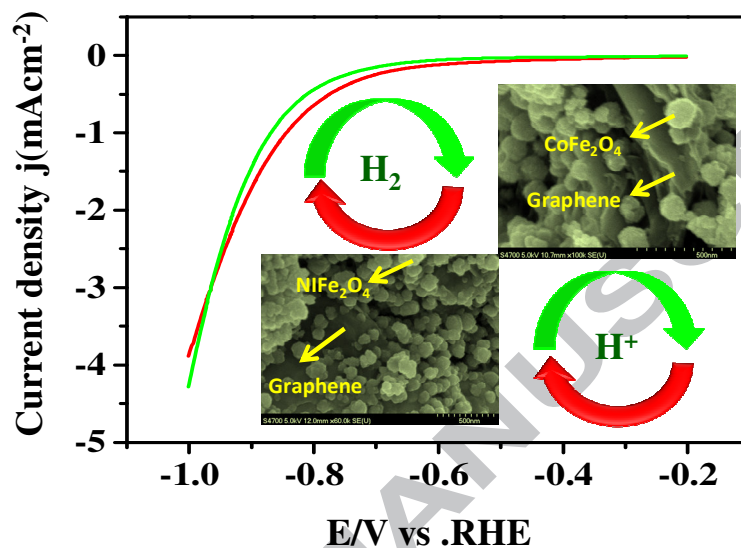
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## Graphical abstract



## High lights

- $\text{CoFe}_2\text{O}_4/\text{Graphene}$  and  $\text{NiFe}_2\text{O}_4/\text{Graphene}$  were synthesized by a simple solvothermal method.
- Hydrogen evolution reaction activities of  $\text{CoFe}_2\text{O}_4/\text{Graphene}$  and  $\text{NiFe}_2\text{O}_4/\text{Graphene}$  nanocomposites shows a high current density
- Enhanced current density due to low onset potential on nanocomposite surface

## Abstract

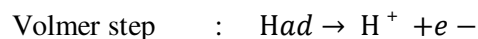
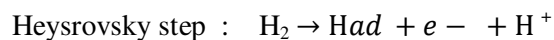
Cobalt and Nickel ferrite based graphene nanocomposites with increased electrochemical performances were successfully prepared by solvothermal process. To know the structure and morphology of the as-synthesized nanocomposite, the material was investigated by X-ray diffraction and electron microscopy techniques. Further, the material was tested for hydrogen production through electrochemical route. HER activity of nanocomposites was tested for hydrogen evolution at an applied potential of -1.2 to 0.8 V in acidic electrolyte. It shows good exchange current density of  $47.9 \text{ mAcm}^{-2}$  and  $41.2 \text{ mAcm}^{-2}$  at over potential of 248.3 mV and 259 mV and a Tafel slope of  $116.6 \text{ mVdec}^{-1}$  and  $121.4 \text{ mVdec}^{-1}$  for CFG and NFG nanocomposite

respectively. The experimental results revealed that cobalt and nickel ferrites based graphene nanocomposites is a good electrocatalyst towards hydrogen production.

**Keywords:** Ferrites, graphene, nanocomposite, electrocatalyst, hydrogen evolution.

## 1. Introduction

In recent days, the consumption of energy throughout the world mainly depends on the fossil fuels such as coal, natural gas and petroleum, but use of the same leads to greenhouse effect thus deteriorating the environment [1]. To reduce the greenhouse and environmental effects, hydrogen is considered as one of the most important energy source having advantages such as high quality, high energy density, clean energy fuel for several devices, environmentally friendly, produced from an abundant renewable energy sources and is certainly a promising energy carrier for the future [2]. Hydrogen can be produced by various methods such as coal gasification, thermolysis, thermal water splitting, hydrocarbon steam reforming, biomass pyrolysis, photolysis and electrolysis [3]. Electrolysis is a good-looking process for hydrogen production because of its simplicity, high efficiency and suitable for large scale production [4-5]. One of the most effective ways for hydrogen production is based on environmental friendly electrocatalytic water splitting. The hydrogen gas produced by the cathode material can possibly be required for the future hydrogen economy, for instance fuel cells, the most promising alternative energy source. [6] The hydrogen evolution reaction (HER), the electrochemical route is of low cost, greater efficiency and ease handling is considered as the most attractive power source for portable electronic device and this is one among the plentitude of fuel cells [7]. Kinetics of HER is not simple as it depends on electrochemical conditions, where in multiple pathways can simultaneously occur. Cathodic hydrogen evolution in acidic aqueous media is accepted to take place in three steps [8].



Hydrogen evolution reaction has been investigated on various electrode materials in view of effective ways of hydrogen production viz. lower potential and favorable kinetic characteristics.

The overall reaction mechanism of the above rapid reaction depends on many imperative kinetic parameter like rate, exchange current density  $i_0$  ( $A/cm^2$ ) at a given temperature/pressure, its corresponding activation energy  $E_a$ (KJ/mol), anodic to cathodic transfer coefficients viz. tafel slope (mVperdecade). All these parameter analysis would determine the type of the reaction viz. Tafel, Volmer and Heyrovsky and these reactions depend on the over potential of  $H_2$  production, which is a key factor governing the reaction. An electrode for the electrochemical hydrogen evolution reaction (HER) should have basic properties such as large active surface area, low over potential, electrochemical stability, selectivity, low cost, ease of use and good electrical conductivity [9-14]. Though advantageous, this method is not cost effective and requires high energy consumption. An imperative factor which influences the cost of this method is the over potential of hydrogen evolution reaction (HER) and hence in order to reduce the production cost, the over potential (potential difference between the reversible reduction potential and practical discharge potential) of HER needs to be decreased by the use of alternative electrocatalytic materials. Many efforts have been done for reducing this overvoltage. The decrease in the over potential could be accomplished by suitable choice of materials with less over potential and high electrocatalytic activity. Platinum cathodes are commonly used for HER and are the most efficient electrocatalyst for HER in acid media with significant rate and almost zero over potential. But the use of Pt as electrode makes the process too expensive for commercialization and hence cannot be used directly as solid materials for industries. In this view, it is imperative to search for alternative catalysts, which are cost effective with high HER activity [14-15]. There are other metallic electrodes reported for water electrolysis but suffer from corrosion effects and consequently have a short lifetime [16]. Various research results revealed that the electrocatalytic activity of the electrodes for HER depends on the integrative influence of diverse factors including electrode composition, surface morphology, support materials etc. Nevertheless, the degradation issue is often ignored when discussing the performance of the electrodes for HER catalysis with the fact that many electrodes with high electrocatalytic activity may not have desired corrosion resistance in practice [17]. The hydrogen evolution reaction [HER] is a cathode based reaction via water electrolysis using a catalyst albeit expensive and the cost can be minimized with the use of cheap and affective catalysts. Thus, non-platinum active metals such as Fe, Ni, Cu, Co as well as their alloys and composites have received a huge attention as electrocatalyst for HER due to their low cost and good activity. Glassy carbon electrodes (GC)

are widely used in electrochemistry in aqueous acid-base medium compared to metallic electrode as it has a long life time. (Because of the over potential to HER with GC, this work has been focused on developing electrocatalyst, which are active, stable and cheap). The hydrogen evolution reaction with graphene based composites deals with low adsorption energy of the reactants/intermediates, yielding to a low catalytic efficiency and high activation barrier. Hence graphene with chemically stable nanoparticles have been used to enhance the kinetics of HER [18-19]. Graphene oxide a two dimensional material has stimulated a large amount of research owing to its unique characteristics such as large specific surface area, excellent electrical conductivity, and great mechanical strength [20]. On the other hand, some of the properties of functional molecules can be significantly improved by adsorbing them onto a graphene support. Recently combination of graphene sheet with inorganic material has been developed to widen the use of graphene. RGO-magnetic hybrids have been developed for wide range of applications, iron-based spinel oxides such as  $\text{Fe}_3\text{O}_4$  and ferrite with general formula  $\text{AFe}_2\text{O}_4$  ( $\text{A} = \text{Zn, Ni, Co, Mn}$ ) with low cost have been extensively studied as anode materials as electro catalysts. Spinel transition metal oxides with two metal elements provide the feasibility to tune the energy density and working voltage by varying the metal content [21-23].  $\text{MFe}_2\text{O}_4$  ( $\text{M} = \text{Co, Ni, Cu, etc.}$ ) constitute an important class of spinel oxides that exhibit a broad range of interesting physical and chemical properties, offering many intriguing advantages such as the rich redox chemistry, good biocompatibility, high electronic conductivity, good superparamagnetic properties, low toxicity, easy preparation, high adsorption ability, low cost, and abundant resources has potential applications in super capacitor, Li ions batteries, semiconductor photo catalysts, biosensor devices and medical applications [24-26]. Such spinel ferrites possess significant electrocatalytic activity and stability in high pH but its low electrical conductivity restricts its application as a catalyst. In general, the practical applications of ferrites mainly depend on electronic conductivity, as a result of thermal activation of electrons or positive holes along the chains of neighboring cations in the ionic lattice [27]. Potential application energy storage Studies have shown that the charge transfer happened via hopping processes between cations of different valencies, which requires relatively lower activation energies [28], wherein O forms the face centered cubic (fcc) packing with M(II) occupying the octahedral (O) interstitial site and Fe(III) distributed evenly in the O and tetrahedral (T) sites. Such a structure has shown good electrical conductivities due to the electron hopping between different valence states of metals in O-sites

and also provides necessary surface redox active metal centers for the adsorption and activation of electroactive species [29-31]. In view of all the above factors, this report has been focused on the development of ferrites with graphene as composite materials and further been tested as an electrocatalyst towards hydrogen evolution reaction (HER). The developed materials was investigated by FESEM, XRD, and TEM to know its structural features and further exploited by various electrochemical tests like cyclic voltammetry, linear sweep voltammetry, electrochemical impedance spectroscopy and tafel analysis to study the effect of the ferrite composites towards HER reaction.

## 2. Experimental

### 2.1 Materials

All the chemicals were of analytical grade and utilized as received without further purification. Graphite fine powder, hydrogen peroxide (30 wt%), sodium nitrate (98%), sulphuric acid (99 wt%), potassium permanganate,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , cobalt chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ), nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ), polyethylene glycol (PEG) and sodium acetate were procured from SIGMA Aldrich and used as received without further purification.

### 2.2 Preparation of $\text{CoFe}_2\text{O}_4\text{-G}$ and $\text{NiFe}_2\text{O}_4\text{-G}$ composites

GO was synthesized from natural flake graphite by a modified Hummers method [32]. Cobalt ferrite and nickel ferrite with graphene composites were prepared by using solvothermal process based on our earlier method.[32] The typical procedure for preparing  $\text{CoFe}_2\text{O}_4\text{-G}$  is as follows: 300 mg of GO, 1.62 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , and 0.714 g  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  were dispersed in 150 mL of ethylene glycol (EG) with ultra-sonication for 2 h. Subsequently, 10.8 g of sodium acetate and 3.0 g polyethylene glycol (PEG) were added, followed by stirring for 30 min. The mixture was then transferred to a Teflon-lined stainless steel autoclave and heated at  $200^\circ\text{C}$  for 10 h. The resultant black product was washed with de-ionized water and ethanol several times by centrifugation and was dried at  $45^\circ\text{C}$  in a vacuum oven.  $\text{NiFe}_2\text{O}_4\text{-G}$  was prepared similarly. The composites  $\text{CoFe}_2\text{O}_4\text{-G}$  and  $\text{NiFe}_2\text{O}_4\text{-G}$  are denoted as CFG and NFG respectively.

### 2.3 Material characterization

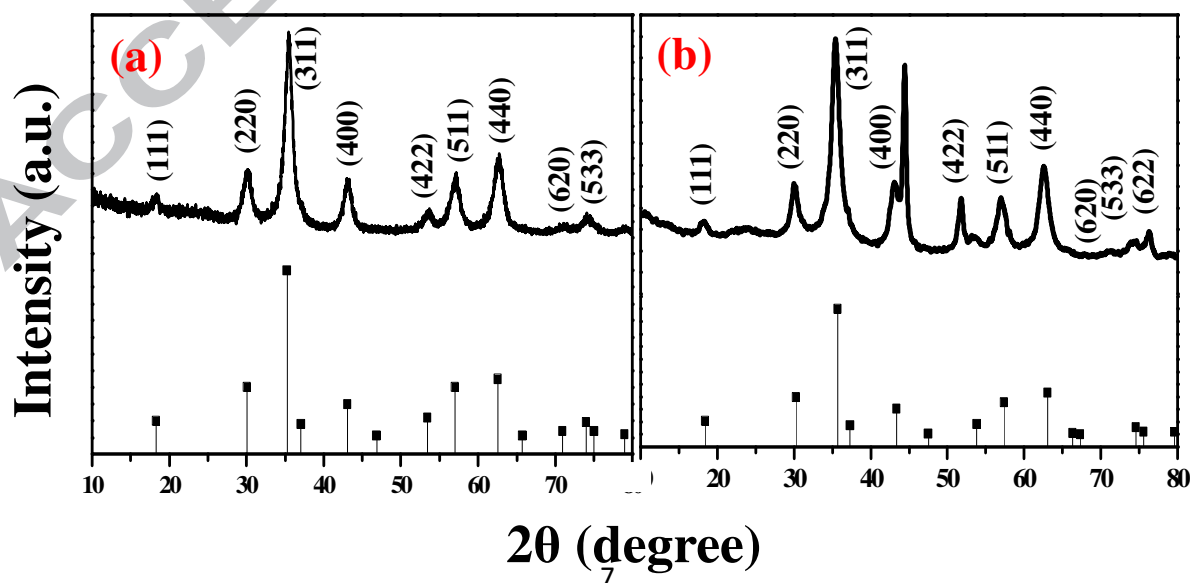
The X-ray diffraction measurements were performed by using a Rigaku Miniflex X-ray diffractometer with Cu K $\alpha$  (1.5406Å<sup>0</sup>) radiation. The surface morphologies and mappings of the nanocomposites were obtained with FESEM by using a Hitachi S-4800 and EDX respectively. The samples were analyzed with high-resolution TEM by using a JEOL-2000EX operated at 120 kV .

## 2.4 Electrochemical Measurements

Electrochemical measurements were performed with a CHI 660C electrochemical workstation. All the experiments were performed at room temperature with a conventional three electrode electrochemical cell setup; Pt wire used as counter electrode, Ag/AgCl as reference and CFG, NFG nanocomposites as working electrodes respectively. The electrochemical measurements were carried out in aqueous solutions, where analytical reagents and doubly distilled water was always used. The test electrolyte was a freshly prepared 0.5M H<sub>2</sub>SO<sub>4</sub> solution. The polarization experiments viz. cyclic voltammetry, linear sweep voltammetry and electrochemical impedance measurements were carried out as test experiments. The potentials were measured against and referred to RHE electrode. The impedance was recorded in the frequency domain of 0.1Hz to 10<sup>5</sup> Hz at an applied voltage of 0.1V. To achieve reproducibility, each experiment was carried out at least twice and average values are reported.

## 3. Results and discussion

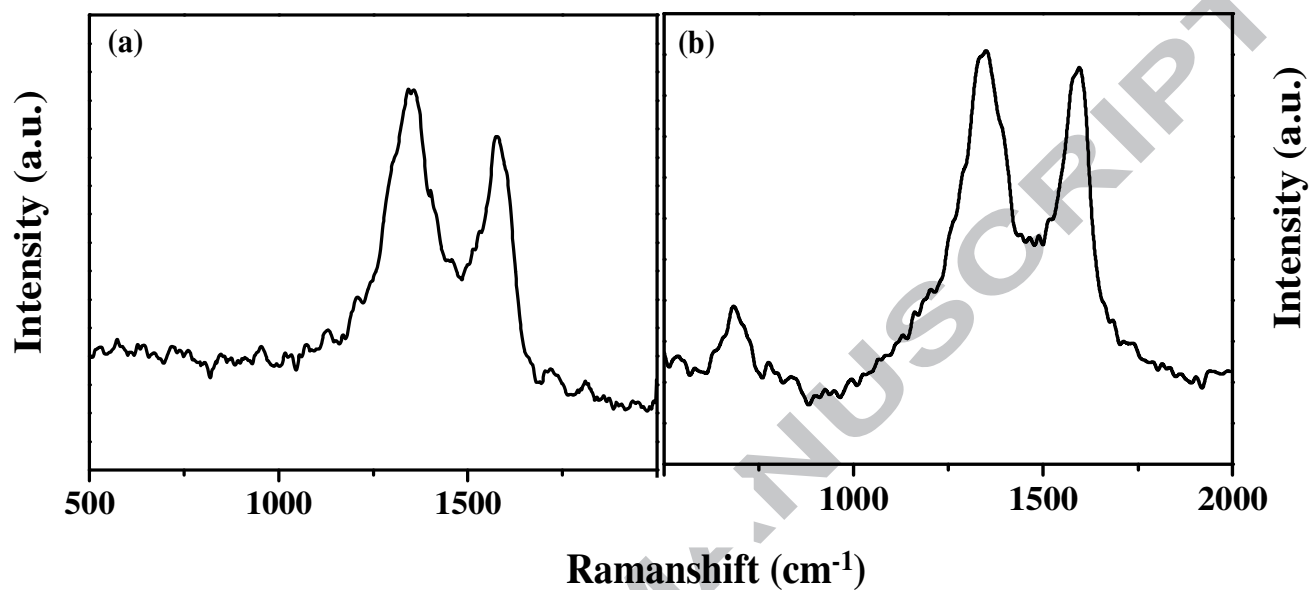
### 3.1 Structural and morphological analysis



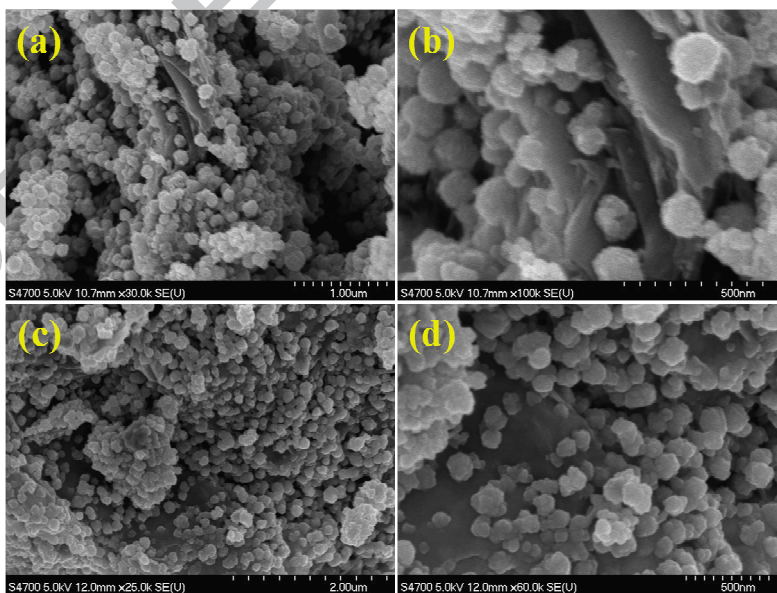


**Fig. 1.** XRD pattern of (a)  $\text{CoFe}_2\text{O}_4\text{-G}$  (CFG) and (b)  $\text{NiFe}_2\text{O}_4\text{-G}$  (NFG)

Fig. 1 shows the X-ray diffraction patterns of  $\text{CoFe}_2\text{O}_4\text{-G}$  (CFG) and  $\text{NiFe}_2\text{O}_4\text{-G}$  (NFG) composites. In Fig. 1a, the crystalline planes (111), (220), (311), (400), (422), (511), (440), (620) and (533) are ascribed to the diffraction peaks at  $2\theta$  values of  $18.34^\circ$ ,  $30.19^\circ$ ,  $35.39^\circ$ ,  $43.11^\circ$ ,  $53.52^\circ$ ,  $57.11^\circ$ ,  $62.66^\circ$ ,  $70.90^\circ$  and  $74.32^\circ$  respectively. All most, all the diffraction peaks of CFG were assigned to the spinel-type  $\text{CoFe}_2\text{O}_4$  in accordance with the standard JCPDS no. 22-1086 (Fig. 1a) [20]. Fig. 1b shows the X-ray diffraction patterns of  $\text{NiFe}_2\text{O}_4\text{-G}$  composites. The diffraction peaks at  $2\theta$  values of  $18.34^\circ$ ,  $30.11^\circ$ ,  $35.57^\circ$ ,  $42.91^\circ$ ,  $53.33^\circ$ ,  $57.11^\circ$ ,  $62.61^\circ$ ,  $70.90^\circ$ ,  $74.32^\circ$  and  $76.29^\circ$  can be ascribed to the crystalline planes of (111), (220), (311), (400), (422), (511), (440), (620) (533) and (622) respectively. It could be seen that almost all the diffraction peaks of NFG were assigned to the spinel-type of  $\text{NiFe}_2\text{O}_4$  in accordance with the standard JCPDS no. 86-2267 (Fig. 1b) [33]. After the reduction of GO to graphene by solvothermal process, the reduced GO sheets were exfoliated and decorated by  $\text{CoFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$  nanoparticles. This process might have led to the disappearance of the diffraction peaks of graphene (002) in accordance with the earlier reports [34]. These samples show spinel structure having  $\text{Oh}^7\text{-Fd}3\text{m}$  space group. The Raman study is a useful tool for graphene based materials. Figure 2 shows two broad peaks centered around  $1,349$  and  $1,576\text{ cm}^{-1}$  for CFG nanocomposite and  $1,337$  and  $1589\text{ cm}^{-1}$  for NFG nanocomposites, which are assigned to the D band and G band of graphene and their relative intensity ( $I_D/I_G$  ratio) relates the quantity of restoration of the  $\text{sp}^2$  carbon. The G band is attributed to the  $\text{E}_{2g}$ -vibration mode, whereas the D band is associated with the  $\text{A}_{1g}$  mode of the small crystallites or boundaries of larger crystallites. The restoration of  $\text{sp}^2$  carbon graphene increases the conductivity [1- 3]. Hence as observed from the figure, well defined peaks shows the interaction between ferrites and graphene, which also contribute to the electron transfer between them. The surface morphology and particle size of the as-prepared ferrite samples were further analyzed by FE-SEM and TEM analysis. From FE-SEM as shown in Fig.3, it was observed that the  $\text{CoFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$  nanoparticles were distributed as homogeneous spherical particles on graphene sheets. Though the particles were homogenous with the estimated cluster size ranging between  $140\text{-}160\text{ nm}$ , they were aggregated as seen from the FE-SEM images.

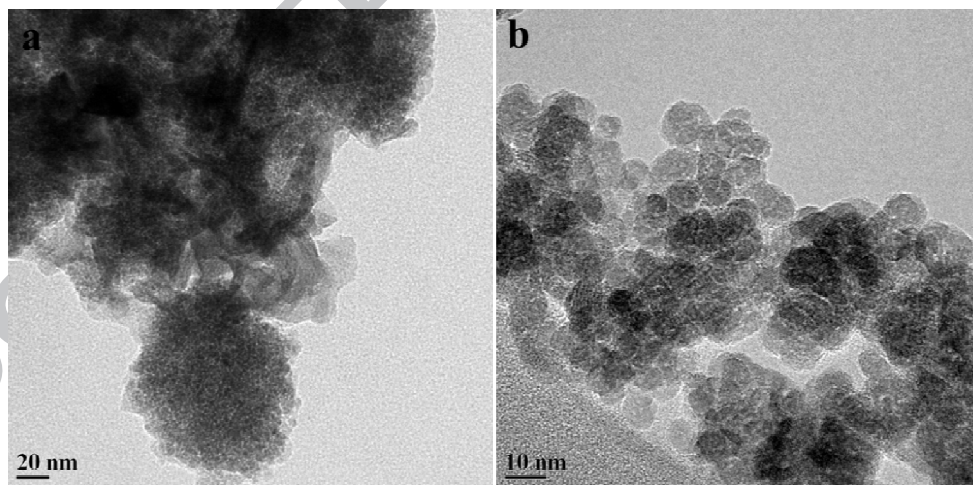


**Fig. 2.** Raman spectra of (a) CoFe<sub>2</sub>O<sub>4</sub>-G (CFG) and (b) NiFe<sub>2</sub>O<sub>4</sub>-G (NFG) nanocomposite.



**Fig. 3.** FE-SEM images of (a,b)  $\text{CoFe}_2\text{O}_4\text{-G}$  (CFG) and (c,d)  $\text{NiFe}_2\text{O}_4\text{-G}$  (NFG) at various magnifications.

Structure of the CFG and NFG composites were further investigated by TEM (Fig. 4). Porous structures are seen in both CFG and NFG but not in graphene. As seen from the image, the  $\text{CoFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$  nanoparticles were actually the aggregation of a great number of smaller nanoparticles with an average size of 10-15 nm and exhibits porous structure.  $\text{CoFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$  spheres were decorated on flake like graphene nanosheets with an average diameter of 150 nm. As observed, though in both the cases, the ferrite particles are distributed homogeneously over the graphene surfaces, the particles are more uniformly shaped and more uniformly aligned in CFG than NFG. Hence it could be confirmed from the above analysis that the solvothermal route offered a homogeneous synthesis of the nanocomposites. The homogeneous distribution of the particles might prevent the stacking of graphene layers. Similar distributions were observed in the case of CFG also. Such a homogeneous distribution of particles could be beneficial for increasing the conductivity allowing fast transport of electrons between the catalyst and the electrodes [35]. Such kind of uniform distribution of ferrite particles over graphene sheets could be an additive factor to increase the catalytic effect towards HER reaction.

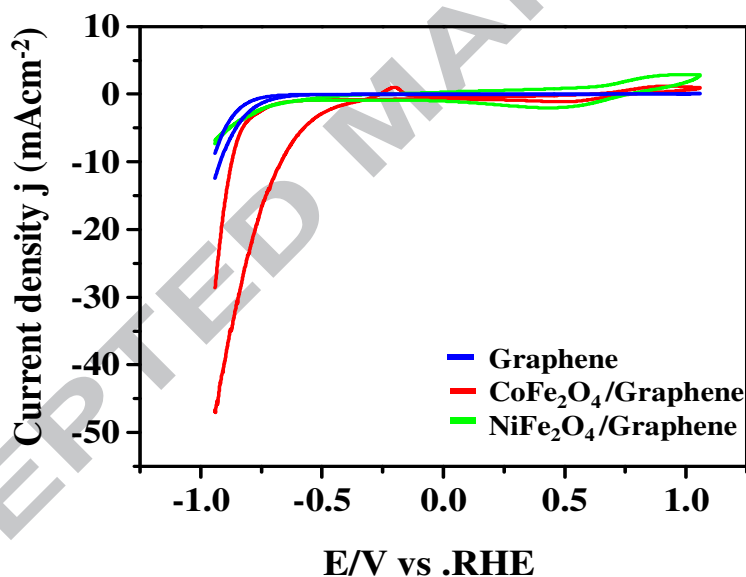


**Fig. 4.** TEM images of (a)  $\text{NiFe}_2\text{O}_4\text{-G}$  (NFG) and (b)  $\text{CoFe}_2\text{O}_4\text{-G}$  (CFG)

## 3.2 Electrochemical hydrogen evolution

### 3.2.1 Voltammetric studies

Cyclic voltammetry (CV) test was chosen for characterization of the prepared composite materials towards hydrogen evolution reaction and the corresponding plots are given in Fig.5. CV curves were recorded from -1.2 to 0.8V at a scan rate of 100 mV/s. As observed from the figure, the rapid increase in the cathodic current was associated with the oxide reduction followed by  $H^+$  intercalation and the corresponding anodic current peak was due to the de-intercalation process [36]. Thus cyclic voltammetry results demonstrated the good catalytic activity of the ferrite based composites for HER reaction. Both the modified electrodes clearly showed an increment in magnitude of current and positive potential shift with respect to the bare electrode, which confirms the electrocatalytic activity of CFG and NFG towards HER.



**Fig. 5.** Cyclic voltammetry of CFG and NFG nanocomposite at a scan rate of 100 mV/S in 0.5 M  $H_2SO_4$

### 3.2.2 Polarization test analysis

To systematically study the electrochemical activity of the catalyst, steady state polarization curves of HER for the catalyst were measured. Polarization is a technique used for the investigation of hydrogen evolution reaction, (HER) which is the production of  $H_2$  gas through

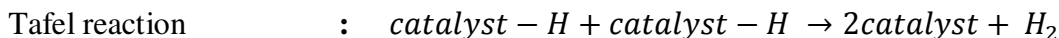
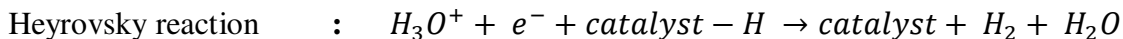
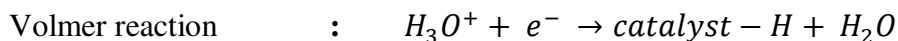
water electrolysis ( $H_2O \rightarrow 2H_2 + O_2$ ) [37]. The electrocatalytic activities of CFG and NFG nanocomposites were evaluated in 0.5M  $H_2SO_4$  using a three probe electrode system and the corresponding polarization curves of the composites are given in Fig. 5 measured at a scan rate of 100mV/s. As observed from the analysis, the onset potential (initial potential for  $H_2$  evolution) of CFG and NFG are -0.979 V and -0.98V respectively, which are comparatively lower than observed for graphene (-1.01 V) and bare GC electrode (-1.06V). Both the composites exhibited a slightly different catalytic activity, which might be due to the electron transfer capability of the nanocomposites. Further extrapolation of the Tafel plot to the current axis gives the exchange current density viz 47.9  $mAcm^{-2}$  and 41.2  $mAcm^{-2}$  for CFG and NFG respectively. Thus the results revealed that both the nanocomposites showed a low onset potential and a rapidly increasing current density within the applied potential [-1.2 to 0.8V]. Thus the good electrocatalytic behavior of the composite materials might arise from the synergetic effect of the exposed active sites provided by the ferrite/graphene composites and graphene, which in turn could promote rapid electron transport.

Tafel plots obtained from over potential versus log current density ( $\eta$  vs.  $\log j$ ) are shown in Fig.6, which could be exploited for the quantitative kinetics analysis of HER. The linear regions of the Tafel plots were fitted into the Tafel equation

$$\eta = a + b \log j$$

$$\eta = \frac{2.3}{\alpha F} \log j_0 - \frac{2.3}{\alpha F} \log j$$

where  $\eta$  is the overpotential,  $j_0$  is exchange current density,  $R$  is the ideal gas constant (8.314 J  $mol^{-1}K^{-1}$ ),  $T$  is the absolute temperature and  $F$  is the Faraday constant. The value of Tafel slope ( $b$ ),  $J_0$  and transfer coefficient ( $\alpha$ ) are given in Table 1. It is generally accepted that there are three principle steps for converting named  $H^+$  to  $H_2$  for HER in acidic medium, commonly named as Volmer, Heyrovsky and Tafel reaction. The former involves the electrochemical reduction steps, the second either an ion or atom reaction and the third is the atom combination reaction. Within a particular set of conditions, when the Volmer reaction is the rate determining step of HER, the Tafel slope is expected to be in the range of 120  $mVdec^{-1}$  (with  $\alpha$ , charge transfer coefficient value being 0.5). When the rate-limiting step is the Heyvosky or the Tafel-step, the slope would be in the vicinity of 40  $mVdec^{-1}$  and 30  $mVdec^{-1}$  with  $\alpha$  value being 1.5 and 2.0 respectively [38] (Scheme 1).



In the case of ferrite based composites, the Tafel slope values were calculated to be  $116.6 \text{ mVdec}^{-1}$  and  $121.4 \text{ mVdec}^{-1}$  for CFG and NFG with cathodic transfer coefficient ( $\alpha$ ) value being 0.51 and 0.49 respectively and hence it could be concluded that the HER mechanism of both the ferrite catalyst follows the Volmer reaction. Compared between CFG and NFG, the latter gave a smaller slope value and hence better electrocatalytically active than CFG but it was a marginal difference and both were electrocatalytically active towards HER. This marginal difference could be attributed to the storage electronic coupling between CFG and graphene, thus causing the difference leading to more efficient electron transport between the catalytic edge sites and the underlying electrode substrate. The calculated values are given in Table 1 for both the composites and the table, it could be observed that a higher charge transfer coefficient and a lower overpotential value was observed for CFG. This could be a cumulative factor of many reasons viz. particle size and its internal resistance.

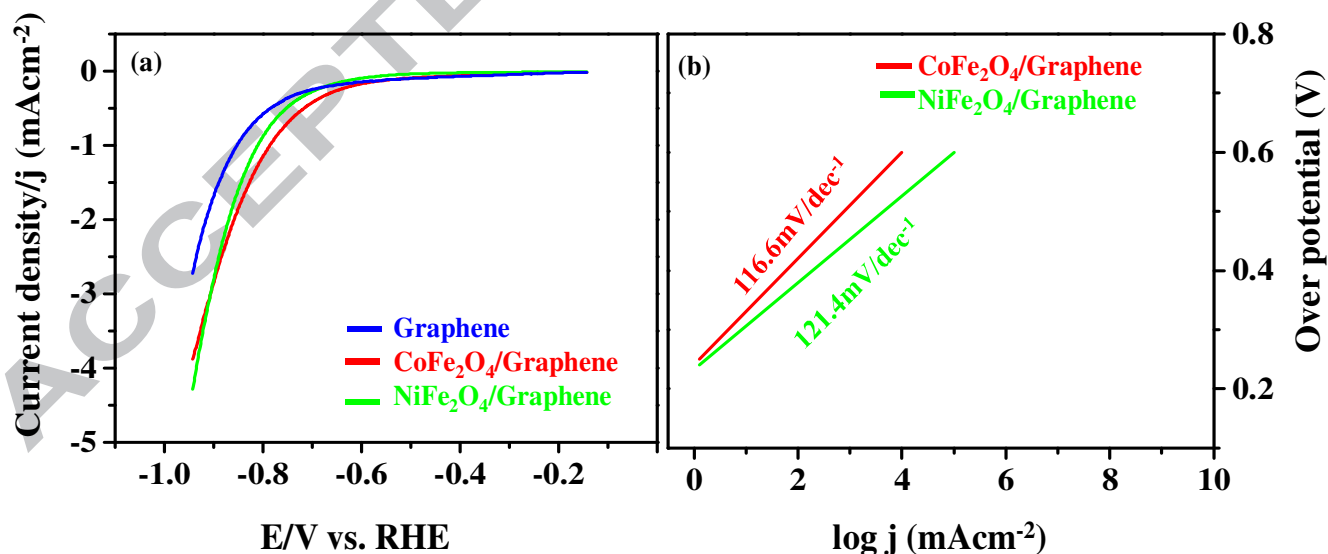


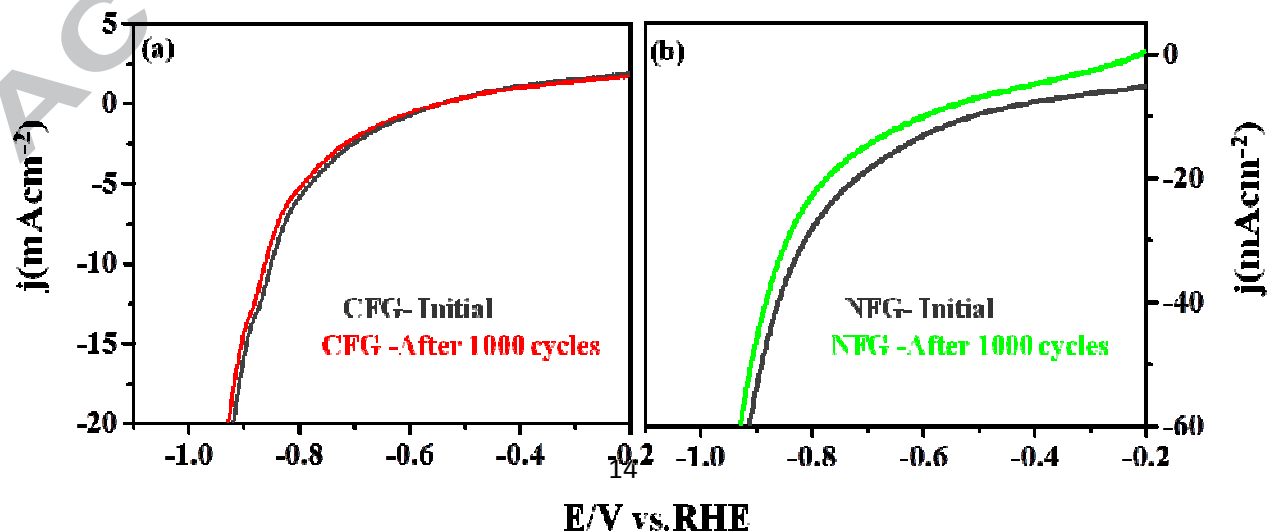
Fig. 6. (a) Linear sweep voltammetry and (b) Tafel plot of CFG and NFG nanocomposite.

**Table: 1** Tafel slopes and Exchange current density values for HER using CFG and NFG nanocomposite

| Catalyst                            | $-\log j_0/\text{mA}/\text{cm}^{-2}$ | $\text{bmV}/\text{dec}^{-1}$ | $\alpha$ | $\eta$ (mV) |
|-------------------------------------|--------------------------------------|------------------------------|----------|-------------|
| CoFe <sub>2</sub> O <sub>4</sub> -G | 47.9                                 | 116.6                        | 0.51     | 248.3       |
| NiFe <sub>2</sub> O <sub>4</sub> -G | 41.2                                 | 121.4                        | 0.49     | 259         |

### 3.2.3 Cycle stability test for Nanocomposite

The long term stability test for nanocomposite was performed and the results are shown in Figure. 7. CFG and NFG catalysts based electrodes were continuously cycled for 1000 cycles in 0.5M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 100 mV/s. The current density remained unchanged even after 1000 cycles for CFG but in the case of NFG, there was a slight decrease though it was marginal. This slight difference is because of H<sup>+</sup> or H<sub>2</sub> bubbles on the surface of the electrode that delays the reaction in both nanocomposites indicating good durability of this catalyst in acid solution.





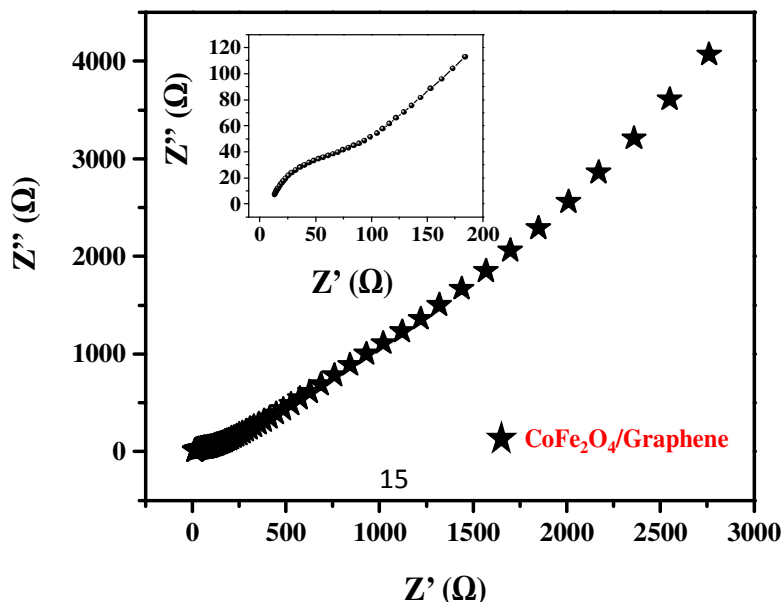
**Fig. 7** Cyclic stability test for (a) CoFe<sub>2</sub>O<sub>4</sub>-G and (b) NiFe<sub>2</sub>O<sub>4</sub>-G in 0.5M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 100 mV/s

### 3.2.4 Electrochemical impedance spectroscopy

To further ratify the electrode kinetics, electrochemical impedance spectroscopy (EIS) was recorded for both the ferrite composites. EIS was performed at a potential of 0.1 V vs. Ag/AgCl and the same is given in Fig. 8 and Fig.9 respectively. In the Nyquist plot, the X and Y axes symbolizes the real and negative imaginary parts of impedance [39-41]. The charge transfer resistances (R<sub>ct</sub>) for hydrogen evolution of NFG are 21.35 Ω and for CFG is 17.36 Ω, which is attributed to the semicircle recorded at the identical over potential at 0.1 V in the frequency range 0.1 Hz to 10<sup>5</sup> Hz. From the frequency (f\*) corresponding to the maximum of the imaginary component (-Im Z'') of the semicircle, the time constant (τ) is calculated using the expression [45]. In this experiment modified electrode/electrolyte interface of the nanocomposite is lower in double layer capacitance and hence increased the charge transfer resistance of hydrogen evolution.

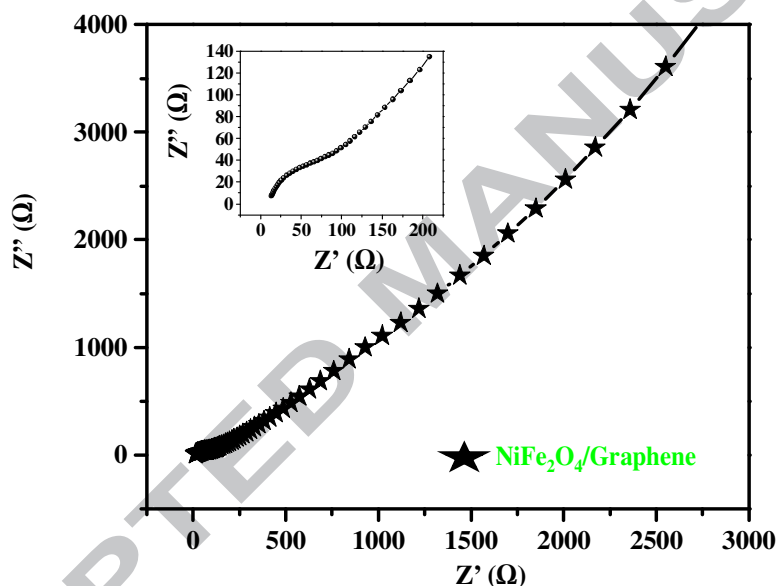
$$\tau = 1/2\pi f^*$$

The time constant was less, and was calculated to be 6.65×10<sup>-5</sup>s and 4.9 ×10<sup>-5</sup>s for CoFe<sub>2</sub>O<sub>4</sub>/G and NiFe<sub>2</sub>O<sub>4</sub>/G nanocomposite respectively.





**Fig:8.** Nyquist plot of CoFe<sub>2</sub>O<sub>4</sub>-Graphene electrodes by applying a sine wave with amplitude of 0.1 V over the frequency range from 0.1 Hz to 10<sup>5</sup>Hz. Inset: Enlargement of the Nyquist plots in high frequency region.



**Fig. 9** Nyquist plot of NiFe<sub>2</sub>O<sub>4</sub>-Graphene electrodes by applying a sine wave with amplitude of 0.1 V over the frequency range from 0.1 Hz to 10<sup>5</sup> Hz. Inset: Enlargement of the Nyquist plots in high frequency region.

#### 4. Conclusion

In conclusion, CoFe<sub>2</sub>O<sub>4</sub>-Graphene and NiFe<sub>2</sub>O<sub>4</sub>-Graphene nanocomposite was synthesized by a simple solvothermal method and further investigated for their electrochemical activity towards hydrogen evolution reaction (HER). Results showed that both the nanocomposites exhibited highly electrocatalytic activity towards HER in acidic medium. An exchange current density of 47.9 mAcm<sup>-2</sup> and 41.2 mAcm<sup>-2</sup> at an over potential of 248.3 mV and 259 mV was observed for

CFG and NFG respectively. A Tafel slope of  $116.6\text{mVdec}^{-1}$  and  $121.4\text{mVdec}^{-1}$  showed that the reaction followed Volmer mechanism. Further EIS measurements showed a less charge transfer resistance for CFG composite and hence overall results indicated that CFG based composite is a better electrocatalyst towards HER reaction than NFG. Thus among the two composites, CFG is slightly better in terms of HER activity. This could be due to many factors like size as observed in the TEM analysis, wherein the ferrite particles are distributed homogeneously over the graphene surfaces, the particles are more uniformly shaped and more uniformly aligned in CFG than NFG. This might be one of the reasons for the fast transport of electrons in the case of CFG and hence better electrocatalytic activity. Hence there is not a much drastic effect with respect to the size of the particles. An additional supporting result is EIS analysis, where the resistance value for NFG and CFG are  $21.35\ \Omega$  and  $17.36\ \Omega$ , which might be due to the difference in electrical conductivity. Thus both  $\text{CoFe}_2\text{O}_4$ -Graphene (CFG) and  $\text{NiFe}_2\text{O}_4$ -Graphene (NFG) nanocomposites as electrocatalyst could be proposed as a good candidate for HER.

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### REFERENCE

1. S .Lewis “Light work with water” *Nature* vol: 414, Pg: 589-590, (2001).
2. R .Solmaz, G. Kardas.” Fabrication and characterization of NiCoZn-M (M: Ag, Pd and Pt) electrocatalysts as cathode materials for electrochemical hydrogen production”. *Int JHydrogen Energy* vol: 36, pg.: 12079-87, (2011).
3. R.M .Navarro, M.A. Pena, J.L.G. Fierro,” Hydrogen production reactions from carbon feedstocks: fossil fuels and biomass”, *Chem. Rev*,vol :107, pg:3952–3991,(2007).
4. M.H. Miles, “Evaluation of electrocatalysts for water electrolysis in alkaline solutions”, *J. Electroanal. Chem. Interfacial Electrochem.* vol:60,pg: 89–96,(1975).
5. C . Lupi, A,DellEra,M . Pasquali, “Nickel-cobalt electrodeposited alloys for hydrogen evolution in alkaline media”, *Int. J. Hydrogen Energy* vol:34, pg:2101–2106,(2009).

6. Y.R. Dar, P. Vijay, M.O. Tadé, R. Datta.,” Improved Tank in Series Model for the Planar Solid Oxide Fuel Cell” *J. Electroanal. Chem.* vol : 50,pg: 1056–1069, (2012).
7. N.S.Lewis, D.G.Nocera,” A Perspective on Forward Research and Development Paths for Cost-Effective Solar Energy” *Chemsuschem* ,vol : 2, pg: 383-386 (2006).
8. AA. Abdul, BH. Hanaa., MA. Abdul Rahim.” Nanostructured Ni/P/TiO<sub>2</sub> composite coatings for electrocatalytic oxidation of small organic molecules”. *J Electroanal Chem* vol; 620, pg: 517-526, (2008).
9. T.Y.Chen, Y.H Chang, C.L .Hsu, K.H .Wei., C.Y. Chiang, L.J. Li,” Comparative study on MoS<sub>2</sub> and WS<sub>2</sub> for electrocatalytic water splitting”, *Int. J. Hydrogen Energy* vol :38, pg:12-32,(2013).
10. RL. Creery. “Advanced carbon electrode materials for molecular electrochemistry”. *ChemRev* vol: 108, pg: 2646–87, (2008)
11. J.L. Tang, Y. Zuo, “Study on corrosion resistance of palladium films on 316L stainless steel by electroplating and electroless plating”, *Corros. Sci.*vol:50, pg.: 2873–2878, (2008)
12. R. S. Sai Siddhartha, “Spot-free catalysis using gold carbon nanotube & gold graphene composite for hydrogen evolution reaction”. *Journal of power Sources* vol: 288,pg:441-450,(2015).
13. S. Wirth, F. Harnisch, M. Weinmann and U. Schroder, “Electrocatalytic H<sub>2</sub> production from seawater over Co, N-codoped nanocarbons” *Nanoscale* , vol:7,pg: 2306-2316,( 2015).
14. M. H. Tang, C. Hahn, A. J. Klobuchar, J. Wellendorff, T. Bligaard, and T. F. Jaramillo, “Nickel–Silver alloy electrocatalysts for hydrogen evolution and oxidation in an alkaline electrolyte”, *PhysChem. Phys.*,vol :16, pg:19250-19257,(2014).
15. J. R. Kitchin, J. K. Norskov, M. A. Barteau and J. G. Chen,” Modification of the surface electronic and chemical properties of Pt(111) by subsurface 3d transition metals” *J. Chem. Phys.*vol: 120, pg: 10240 (2004)
16. J. O. M. Bockris and E. C. Potter, “The Mechanism of the Cathodic Hydrogen Evolution Reaction” *The Electrochemical Society* , vol: 99, pg no : 169-186,(1952).
17. C. Saby, B. Ortiz, Y. Champagne, and D. Langier “Electrochemical Modification of Glassy Carbon Electrode”. *Langmuir* vol: 13, pg 6805-6813, (1997).

18. W. C. Sheng, H. A. Gasteiger and Y. Shao-Horn, "Hydrogen Oxidation and Evolution Reaction Kinetics on Platinum: Acid vs Alkaline Electrolytes" *J. Electrochem. Soc.*, vol:157, pg:1529. (2010),
19. KS. Novoselov, AK. Geim, SV. Morozov, D. Jiang, Y. Zhang SV, Dubonos, "Electric field effect in atomically thin carbon films". *Science*; vol:306, pg : 5696-666 ,(2004).
20. Y. K .Kim,.; S. W. Han,; D. H. Min, "Graphene Oxide Sheath on Ag Nanoparticle/Graphene Hybrid Films as an Antioxidative Coating and Enhancer of Surface-Enhanced Raman Scattering". *ACS Appl.Mater. Interfaces*, vol : 4, pg :6545–6551,(2012).
21. HY .Koo, HJ. Lee, HJ .Go , YB .Lee, TS. Bae, JK. Kim," Graphene-based multifunctional iron oxide nanosheets with tunable properties". *Chem Eur J* ,vol: 7(4), pg:1214–91 , (2011)
22. SH .Sun, H. Zeng, DB. Robinson, S. Raoux, PM .Rice, SX. Wang, et al. "Monodisperse  $MFe_2O_4$  ( $M = Fe, Co, Mn$ ) nanoparticles". *JAm Chem Soc*, vol :126(1):273–9,(2004).
23. H .Jabeen, V .Chandra, S. Jung, JW. Lee, KS .Kim, SB .Kim."Enhanced Cr(VI) removal using iron nanoparticle decorated graphene". *Nanoscale* vol : 3(9) ,pg: 3583–595, (2011).
24. H.Cheng Lu, J. Chang, W.Wa Vong, H-Ta Chen and Y. Chen,"Porous ferrite synthesis and catalytic effect on benzene degradation." *Int. J. Phys. Sci.* vol : 6 (4), pg : 855–865,( 2011).
25. R.-S. .Gaikwad, "Cobalt ferrite Nano crystallites for sustainable hydrogen production application". *Int. J. Electrochem.*,vol: 6, pg:7291-41, (2011).
26. P. Lavela, J.L. Tirado  $CoFe_2O_4$  and  $NiFe_2O_4$  synthesized by sol-gel procedures for their use as anode materials for Li ion batteries " *journals power sources*" Vol:172 pg.: 379-387(2007).

ACCEPTED

27. B. Cui, H. Lin, J.-B. Li, X. Li, J. Yang and J. Tao, "Core–Ring Structured NiCo<sub>2</sub>O<sub>4</sub> Nanoplatelets: Synthesis, Characterization, and Electrocatalytic Applications" *Adv. Funct. Mater.*, vol :18, pg: 1440–1447 (2008).
28. V. Neburchilov, H.Wang, J. Martin, J. J. & Qu," A review on air cathodes for zinc-air fuel cells". *J. Power Sources* vol:195, pg.1271–1291 (2010).
29. F. Cheng, J. Shen, B. Peng, Y. Pan, Z. Tao and J. Chen,"Rapid room-temperature synthesis of nanocrystalline pinels as oxygen reduction and evolution electrocatalysts"*Nat.Chem.*, , vol: 3, pg: 79–84,(2011). Q.Y. He, S.X. Wu, Z.Y. Yin, H. Zhang, "Graphene-based electronic sensors", *Chem.Sci.*vol ;3pg ;1764,(2012).
30. S .Park, RS .Ruoff. "Chemical methods for the production of graphenes". *Nat Nanotechnol* vol;4(4),pg:217–24. (2009).
31. W.S. Hummers, R.E. Offeman, "Preparation of graphitic oxide", *J. Am. Chem. Soc*vol;80 pg 1339. (1958).
32. P. Kollu, S. Prathapani, E. K. Varaprasadrao, C. Santosh, S. Mallick, A. Nirmala Grace and D. Bahadur, "Anomalous magnetic behavior in nanocomposite materials of reduced graphene oxide-Ni/NiFe<sub>2</sub>O<sub>4</sub> "*Appl. Phys. Lett.*, vol:105, pg:52412,( 2014).
33. Y. S. Fu and X. Wang, "Magnetically separable reduced grapheneoxide/iron oxide nanocomposite materials for environmental remediation Ind." *Eng. Chem. Res.*, vol:50, pg:7210– 7218(2011).
34. Y. Xiao, X. Li , J. Zai , K. Wang , Y. Gong , B. Li Q. Han ,X. Qian "CoFe<sub>2</sub>O<sub>4</sub>-Graphene Nanocomposites Synthesized through An Ultrasonic Method with Enhanced Performances as Anode Materials for Li-ion Batteries" *Nano-Micro Lett.* Vol:6 pg :307–315(2014)
35. AJ. Bard, LR. Faulkner." *Electrochemical methods: fundamentals and applications*". 2nd ed. John Wiley & Sons, Inc.vol:18,pg: 864;( 2001).
36. R. Ganesan, J.S. Lee, "An electrocatalyst for methanol oxidation based on tungsten trioxide microspheres and platinum", *Journal of Power Sources* vol: 217 pg:157 (2006).
37. S.H. Baeck, K.S. Choi, T.F. Jaramilo, G.D. Stucky, E.W. McFarland, "Enhancement of photocatalytic and electrochromic properties of electrochemically fabricated mesoporous WO<sub>3</sub> thin films", *Advanced Materials* ,vol : 15,pg :1269. (2003)
38. X. Xia, X. Zhao, W. Ye, C. Wang. Highly porous Ag-Ag<sub>2</sub>S/MoS<sub>2</sub> with additional active sites synthesized by chemical etching method for enhanced electro catalytic hydrogen evolution. *Electrochimica Acta* 142 (2014) 173–181.
39. Los P, Rami A, Lasia," Hydrogen evolution reaction on Ni–Al electrodes". *J Appl Electrochem* vol: 40, pg:23-135, (1993).

40. Cardona, E. Ortega, J. García Antón, V .Pérez-Herranz.” Assessment of the roughness factor effect and the intrinsic catalytic activity for hydrogen evolution reaction on Ni-based electrodeposits”. *In J Hydrogen Energy* vol;36,pg:9428–38, (2011).
41. D.H. Youn, S. Han, J.Y. Kim, J.Y. Kim, H. Park, S.H. Choi, J.S. Lee, “Highly active and stable hydrogen evolution electrocatalysts based on molybdenum compounds on carbon nanotube-graphene hybrid support”, *ACS Nano* vol: 8, pg: 5164., (2014).

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