

## Effect of Graphene Oxide on the Electrocatalytic Activity of Ni-W Alloy Coating

Liju Elias and  
Ampar Chitharanjan Hegde

Electrochemistry Research Lab,  
Department of Chemistry, National  
Institute of Technology, Surathkal,  
Karnataka, India

### Abstract

Nickel-Tungsten-reduced Graphene Oxide (Ni-W-rGO) composite coating was developed through composite electrodeposition method, and its electrocatalytic activity for alkaline hydrogen evolution reaction (HER) was studied. The development of composite coating with a homogeneous dispersion of rGO nanosheets was achieved from an optimal Ni-W plating bath loaded with graphene oxide (GO), synthesized through the chemical oxidation of graphite. The electrocatalytic efficacy of the composite coating for HER was tested using cyclic voltammetry (CV) and chronopotentiometry (CP) techniques in 1.0 M KOH medium. A remarkable increase in the HER activity was observed for the Ni-W-rGO composite coating compared with the Ni-W alloy coating. The variation in composition, surface morphology and crystal structure of the composite coating effected by the incorporation of rGO into the alloy matrix favor the enhanced HER activity, as evidenced by energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM) and X-ray diffraction (XRD).

**Keywords:** Electrodeposition; Ni-W-rGO composite coating; HER; SEM; XRD study

**Corresponding author:**  
Ampar Chitharanjan Hegde

✉ acrhegde@gmail.com

Electrochemistry Research Lab, Department  
of Chemistry, National Institute of  
Technology, Srinivasnagar-575 025,  
Surathkal, Karnataka, India.

**Tel:** +919980360242

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### Introduction

Hydrogen is widely accepted as the green alternative to the fossil fuel [1-3]. However, the major portion of worldwide hydrogen production is still dependent on the hydrocarbon sources leading to the emission of huge amount of greenhouse gases [2,3]. The production of H<sub>2</sub> from such hydrocarbon sources is neither environmentally benign nor sustainable in the long run [1]. In this context, water splitting has been emerged as an ideal method for the production of high purity H<sub>2</sub> [1-6]. Water electrolysis is a pollution free simple process utilizing the abundant and cheaply available water as the feedstock [2-4]. Whereas, the high energy consumption (overvoltage) for water splitting impedes its wide application [3]. Activation polarization, the major reason for the high overvoltage can be controlled by the selection of good electrode materials [4-6]. The development of noble metal free electrode materials for electrocatalytic hydrogen evolution reaction (HER) is a great challenge to make water electrolysis economically more viable [3-6]. In this regard, Ni based alloys and its composites are attractive due to their intrinsic catalytic activity and cost effectiveness [3-6]. Hence, the alloying Ni with hard and high melting transition metal, namely W can offer better corrosion resistance and electro catalytic efficiency for alkaline water electrolysis.

Composite coatings are found to be a very auspicious and briskly developing field of great importance, both in research and practical applications [7-10]. The rigorous development of the composite coating technology allows the production of metal matrix coatings with various homogeneously dispersed phases, which can impart synergistic properties of the matrix and the guest material [9,10]. Metal/alloy- graphene composite is one of the most promising composite coatings among this class of materials due to its attractive anticorrosion [8], tribological [11] and electrocatalytic [12,13] properties. Whereas, the poor dispersiveness of graphene due to its low density making it difficult to synthesize a metal/alloy-graphene composite through conventional metallurgical methods [11]. In this regard, electrodeposition becomes an effective technique to produce this type of composite coatings through the electrochemical reduction of water dispersible graphene oxide (GO) [14]. This is considered as one of the most simple and economically feasible methods for the fabrication of functional composite coatings for various application [11,15].

In the present investigation, we are developing Nickel-Tungsten-reduced Graphene Oxide (Ni-W-rGO) composite coating as an efficient electrocatalytic material for alkaline HER through the codeposition of homogeneously dispersed GO. The electrocatalytic efficacy of the composite coating is compared

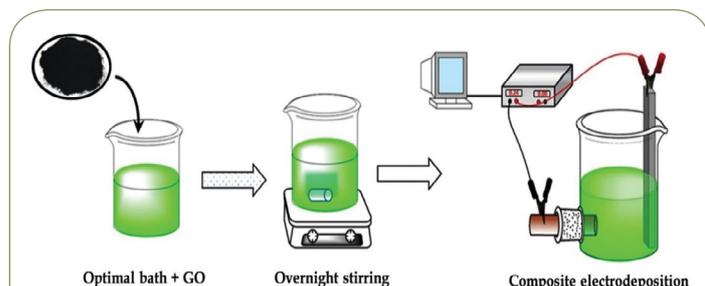
with the conventional alloy coating to ensure the improvement after the incorporation of reduced graphene nanosheets into the alloy matrix.

## Experimental

The deposition of electroactive Ni-W alloy coatings and their characterization were reported elsewhere [16,17]. Further, graphene oxide (GO) was synthesized using modified Hummer's method as reported by Su et al. [18] and added to the optimal plating bath to study the effect of GO on coating characteristics. The formation of GO after the chemical treatment of graphite was confirmed using various characterization techniques such as Raman spectroscopy (Bruker Senterra R200), X-ray diffraction (XRD, Rigaku Miniflex 600, with  $\text{CuK}\alpha$  radiation as the X-ray source) and transmission electron microscopy (TEM, JEOL, JEM-2100). A small amount GO ( $0.5 \text{ g L}^{-1}$ ) was added into the plating for getting it deposited as reduced graphene oxide (rGO) to develop Ni-W-rGO nanocomposite coating. The GO added into the plating bath was dispersed homogeneously through overnight stirring and used directly for deposition on copper rod of  $1 \text{ cm}^2$  effective surface area. The deposition was performed in a custom made 250 mL glass setup using the pre-cleaned copper rod as cathode and Ni as anode. A schematic of the composite electrodeposition process is shown in **Figure 1**. The composite coating was developed at an optimal current density of  $4.0 \text{ A dm}^{-2}$ , as obtained from our earlier study [17]. The alloy and composite depositions were carried out for the same duration of time (600 s), using DC power source (Agilent-N6705A). The developed alloy and composite coatings were characterized by their surface appearance, composition and phase structure using scanning electron microscopy (SEM, JSM-7610F from JEOL, USA), energy dispersive spectroscopy (EDS) and XRD, respectively. The thickness of the alloy and composite coatings was measured using coating thickness gauge (Coatmeasure M and C) and confirmed SEM cross-sectional analysis.

## Electrochemical characterization

The electrochemical characterization of the alloy and composite coatings were carried out using a Potentiostat/ Galvanostat, Biologic SP-150 (Biologic Science Instruments, France). The electrocatalytic activity of the coatings towards alkaline HER was studied in a home made water splitting study setup as shown in **Figure 2**. A three-electrode system with alloy coated substrate as working electrode, platinized platinum of same area as a counter electrode and saturated calomel electrode (SCE) as reference,



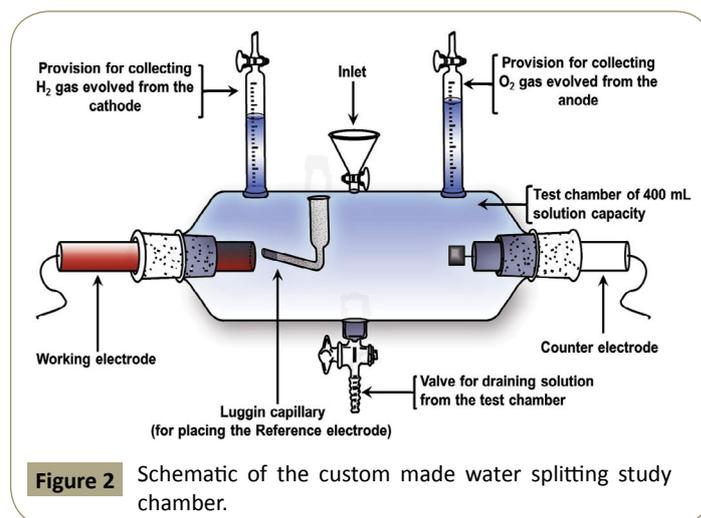
**Figure 1** The schematic of Ni-W-GO composite electrodeposition process.

was made to perform the electrochemical study. Electrochemical analysis such as cyclic voltammetry (CV, recorded within a potential range of 0 to  $-1.6 \text{ V}$ ) and chronopotentiometry (CP, recorded for 1800 s by applying a constant current density of  $-300 \text{ mA cm}^{-2}$ ) were carried out to examine the stability and activity of the test electrodes in  $1.0 \text{ M KOH}$  medium.

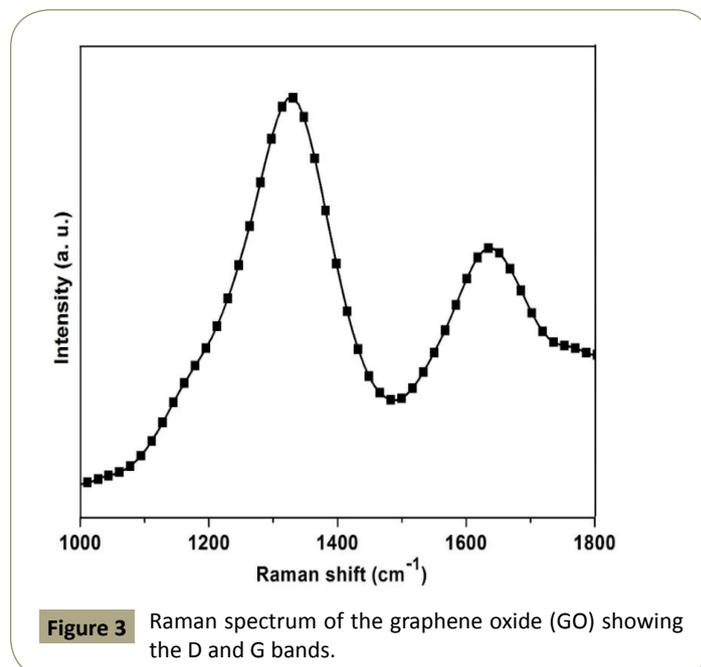
## Results and Discussion

### Characterization of graphene oxide

The synthesized GO nanosheets were characterized using various instrumental methods of analysis. The obtained GO was examined using Raman spectroscopy, an invaluable technique to obtain the structure, crystallization and defects of carbon materials [11,18]. The Raman spectra of the obtained GO nanosheets are given in **Figure 3**. The presence of two peaks at  $1318$  and  $1610 \text{ cm}^{-1}$ , characteristics of the D and G bands corresponds to  $E_{2g}$  phonon of  $\text{sp}^2$  C atoms and carbon lattice defects, respectively [11,13,18].



**Figure 2** Schematic of the custom made water splitting study chamber.



**Figure 3** Raman spectrum of the graphene oxide (GO) showing the D and G bands.

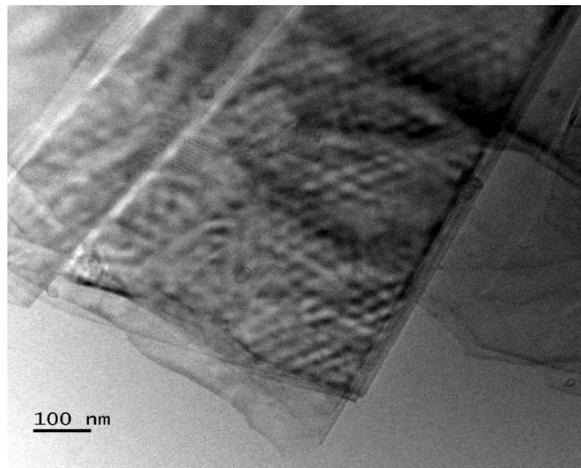
The formation of GO is also confirmed by the XRD analysis. **Figure 4** shows the XRD pattern obtained for the synthesized GO nanosheets. The absence of characteristic reflection of graphite ( $2\theta=26^\circ$ ) and the presence of a reflection at  $2\theta=10.4^\circ$ , with  $d$  spacing of 0.68 nm, due to the intercalation of oxygen confirms the formation of GO [18-20].

Further, the structural characterization of GO nanosheets was performed using TEM analysis (**Figure 5**). The obtained TEM image clearly depicts the rippled and entangled GO nanosheets. The presence of single nanosheets is also evident from the TEM image as shown in **Figure 5**. All these characterizations confirm the formation of GO after the chemical treatment of graphite, and it was used for the preparation of Ni-W-rGO nanocomposite coating.

### Characteristics of Ni-W-GO composite coating

**SEM study:** The surface appearance of the alloy and composite coatings were examined using SEM and the obtained images are shown in **Figure 6**. The alloy coating was found to be almost flat with full of micro-cracks on the surface [17]. Whereas, the composite coating was observed to have homogeneous nodular growths along with the micro-cracks on the surface. The variation in surface appearance of the composite coating compared with the optimal alloy coating is attributed to the incorporation of GO nanosheets into the alloy matrix. Further, the change in surface morphology of the composite coating is ascribed to the increase in W content in the coating effected from the addition of GO into the plating bath. The increase in W content is evident from the EDS analysis results as tabulated in **Table 1**. The micro-cracks on the alloy and composite coatings are attributed to the hydrogen embrittlement and also due to the inherent brittle nature of W [17,21].

**XRD analysis:** The phase structure of the alloy and composite coatings were analyzed using XRD technique and the obtained XRD pattern are given in **Figure 7**. The distinct variation in

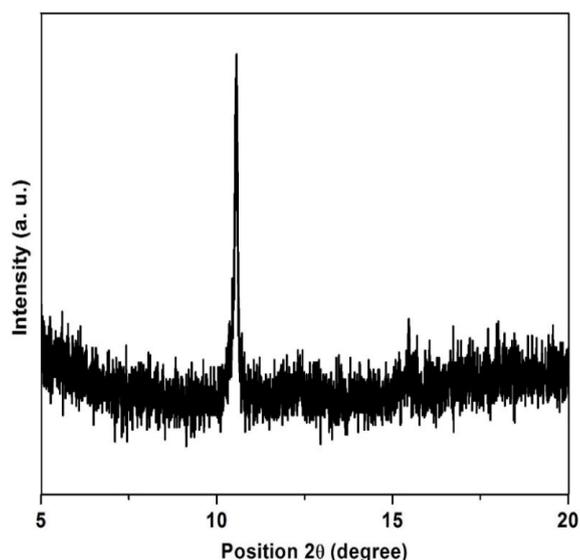


**Figure 5** TEM image of the synthesized graphene oxide.

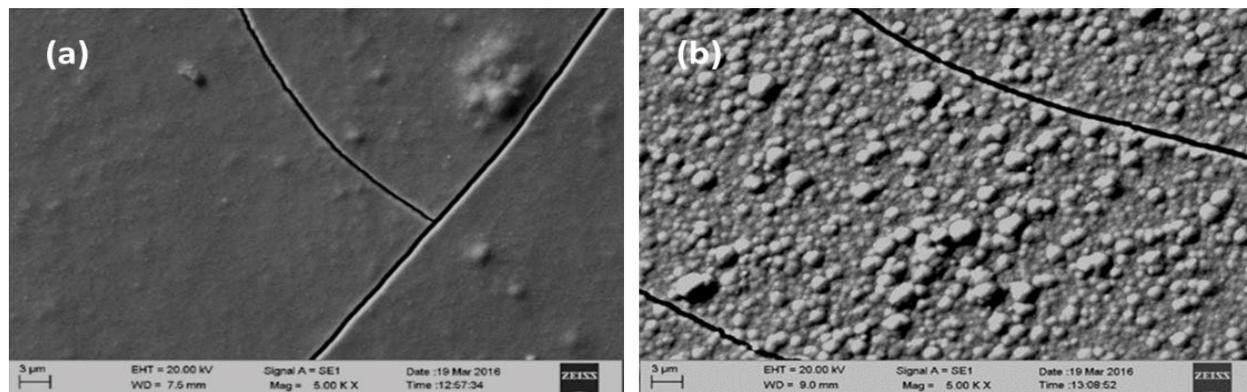
reflections of composite coating the alloy coatings confirms the variation in composition and thereby the variation in the crystal structure of the composite obtained after the incorporation of GO into the alloy matrix. The direction of crystal growth in the composite coating was observed to be changed to W rich (220) plane than the (111) plane in the alloy [17,21]. Further, there was a small shift in the positions of main peak reflections of the composite coating compared with the alloy coating [17]. This shift in peak positions is attributed to the incorporation of GO and thereby the increased W content in the composite coating as compared with alloy coating. The refinement in grain size leading to the formation of nodular growths on the composite surface is also evident from the peak broadening effect, observed in the composite coating [18,20,22]. The presence of (002) peak at  $2\theta=26.4^\circ$  confirms that the GO is deposited as reduced graphene nanosheets into the alloy matrix [11,14,20]. Further, the W rich composite coating resulted in the formation of new reflections corresponds to the W rich phases. It may also note that the intensity of the peaks present in the alloy coating was found to be decreased or disappeared in the composite coating along with the formation of new reflections.

### Effect of GO on coating properties

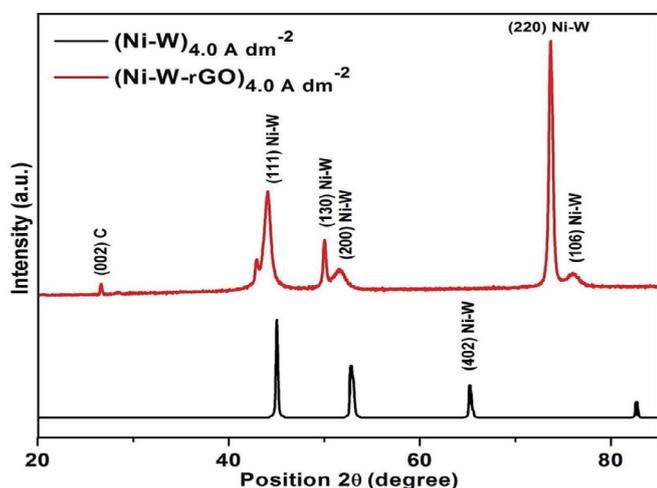
The addition of GO into the plating bath was found to influence the coating properties to a greater extent. The composite electrodeposition leading to the formation of Ni-W-GO nanocomposite coating was found to be effective in enhancing the W content in the coating. The codeposition of the GO as rGO nanosheets along with the metal ions increased the effective surface area for deposition and thereby triggered the enhanced deposition also onto the surface of incorporated graphene nanosheets [23,24]. This type of enhanced deposition activated by the reduced graphene sheets intersticed in the alloy matrix resulted in the formation of W rich composite coating. The effect of incorporated rGO on the coating properties such as composition, thickness, microhardness and appearance are given in **Table 1**. The alloy and composite coatings were found to be bright in visual observation. The thickness and microhardness of the composite coating were also found to be increased in the composite coating with an increase in W content in the coating.



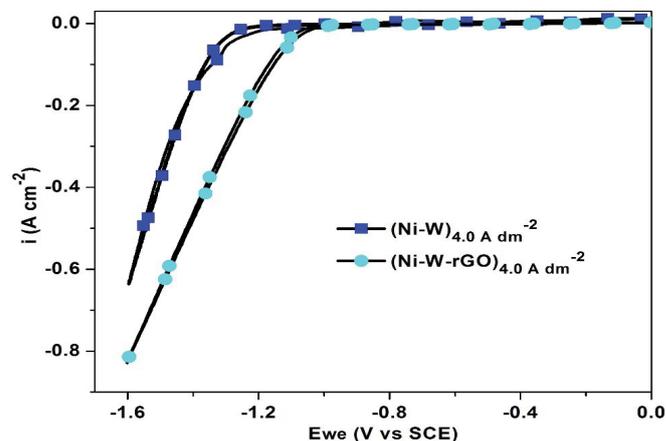
**Figure 4** XRD pattern of graphene oxide showing the presence of (101) reflection at  $2\theta=10.4^\circ$ .



**Figure 6** The SEM images of the coatings developed at  $4.0 \text{ A dm}^{-2}$ : a) Ni-W alloy coating and, b) Ni-W-rGO composite coating.



**Figure 7** The XRD pattern obtained for Ni-W alloy coating and Ni-W-rGO composite coating.

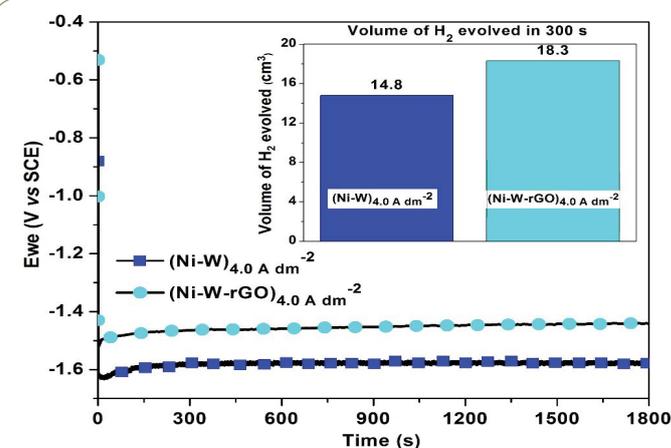


**Figure 8** CV curves showing significant variation in peak current density and onset potential for Ni-W-rGO composite coating compared with Ni-W alloy coating.

## Electrocatalytic activity for alkaline hydrogen production

**Cyclic voltammetry analysis:** The activity of the alloy and composite test electrodes towards alkaline HER was studied using CV analysis. The current-voltage responses obtained from the CV analysis for alloy and composite coatings are shown in **Figure 8**. The remarkable variation in cathodic peak current density ( $i_{pc}$ ) and onset potential obtained for composite coating suggests the enhancement in HER activity after the incorporation of reduced graphene oxide nanosheets. The Ni-W-rGO composite coating was observed to have the maximum current response with minimum onset potential for  $\text{H}_2$  as the data given in **Table 2**. The increase in  $i_{pc}$  value from  $-0.66 \text{ A cm}^{-2}$  for alloy to  $-0.83 \text{ A cm}^{-2}$  for Ni-W-rGO confirms the improvement in HER activity [25-28]. At the same time, the onset potential was also found to become nobler in the composite coating ( $-1.03 \text{ V}$ ) as compared with the alloy coating ( $-1.21 \text{ V}$ ).

**Chronopotentiometry analysis:** The robustness of the alloy and composite test electrodes for alkaline HER was studied using CP analysis by applying a constant current density of  $-300 \text{ mA cm}^{-2}$ , for



**Figure 9** CP responses and the corresponding amount of  $\text{H}_2$  gas evolved during the first 300 s of analysis (in the inset) shows a remarkable improvement for composite coating as compared with the alloy coating.

1800 s. The amount of hydrogen evolved during the first 300 s of analysis from each test electrodes were quantified to relate the

**Table 1** The properties of the alloy and composite coating developed from the same bath under optimal conditions.

| Coatings developed at 4.0 A dm <sup>-2</sup> | Wt.% of W in the deposit | Wt.% of C in the deposit | Thickness of the coating (μm) | Vicker's microhardness V <sub>100</sub> (GPa) | Nature of the deposit |
|--|--------------------------|--------------------------|-------------------------------|---|-----------------------|
| Ni-W-rGO composite coating                   | 22.4                     | 3.1                      | 16.1                          | 3.91  | Bright                |
| Ni-W alloy coating                           | 12.4                     | ---                      | 15.9                          | 3.22  | Bright                |

**Table 2** The alkaline hydrogen evolution parameters of Ni-W alloy and Ni-W-rGO composite coating obtained from CV and CP analysis.

| Coating developed at 4.0 A dm <sup>-2</sup> | Cathodic peak c.d. (A cm <sup>-2</sup> ) | Onset potential for H <sub>2</sub> evolution (V vs SCE) | Volume of H <sub>2</sub> evolved in 300 s (cm <sup>3</sup> ) |
|---|--|---|--|
| Ni-W-rGO composite coating                  | -0.83                                    | -1.03   | 18.3   |
| Ni-W alloy coating                          | -0.66                                    | -1.21   | 14.8   |

efficiency in terms of practical activity. The obtained CP curves and the amount of H<sub>2</sub> evolved from each test electrodes are given in **Figure 9**.

The CP response of the composite coating shows a significant variation in terms of both potential and volume of H<sub>2</sub> gas evolved during the analysis. The observed results suggest the composite coating as an efficient electrode material for alkaline hydrogen production as compared with the alloy coating. The corresponding parameters obtained for alkaline HER from CV and CP analysis are given in **Table 2**. The robustness of the composite electrode under the alkaline water splitting condition is evident from the obtained stable curve and the continuous evolution of hydrogen. The enhancement in electrocatalytic efficiency of the Ni-W-rGO composite coating may be attributed to the increased W content in the composite coating along with the increased surface area [12,24,26,28]. The deposition of the added GO as rGO by reduction during the electrodeposition process, as evident from the (002) peak in the XRD analysis (**Figure 7**), is ascribed to the increased surface area of the composite coating [11,14]. The influence of this deposited rGO on the induced codeposition of reluctant metal 'W', leading to the variation in composition, crystallographic orientation, surface morphology and thereby the electrocatalytic activity of the composite coating [12]. The W content in the Ni-W-rGO composite coating used in the present study is 22.4%. The Ni-W alloy having still higher wt. % of W is found to exhibit increased corrosion resistance [29] and

electrocatalytic activity [21]. Hence, the observed drastic increase of H<sub>2</sub> evolution on Ni-W-rGO composite coating is the combined effect of both increased W content and increased surface area due to rGO incorporation [21,26,28].

## Conclusions

1. Ni-W-rGO composite coating was developed successfully from a GO loaded optimal Ni-W plating bath through electrodeposition method.
2. The composite electrodeposition of the Ni-W-rGO from the optimal bath loaded with GO was found to influence the induced codeposition of the reluctant metal 'W' leading to the formation of a W rich composite coating.
3. The developed Ni-W-rGO composite coating was found to be an efficient electrode material for alkaline HER, evidenced by CV and CP analysis.
4. The drastic improvement in the electrocatalytic activity of the composite coating compared with the conventional alloy coating is attributed to the compositional, structural and morphological changes, resulted from the addition of GO into the plating bath.

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