

## Electro-catalytic Behavior of High Entropy Alloy-graphene (HEA:G) Composite

R. Ashwini<sup>1</sup>, M.Y. Rekha<sup>2</sup>, M.S. Santosh<sup>3</sup>, Chandan Srivastava<sup>4</sup>.

<sup>1</sup>CIIRC, Jyothy Institute of Technology, Bengaluru, Karnataka, India.

<sup>2</sup>Dept. of Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, AL, USA

<sup>3</sup>CSIR – Central Institute of Mining and Fuel Research (CIMFR), Dhanbad, Jharkhand, India.

<sup>4</sup>Dept. of Materials Engineering, IISc, Bengaluru, Karnataka, India.

\* Corresponding author: ashwiniravi23@gmail.com

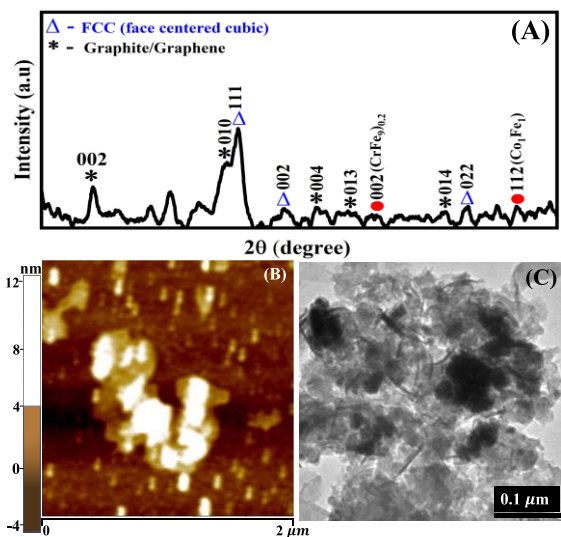
High entropy alloy (HEA) nanoparticles composed of five or more elements in nearly equimolar concentrations are gaining attention due to their excellent thermal, electrical and catalytic behavior [1]. The application of HEA as a heterogeneous catalyst in energy conversion applications exhibit substantially enhanced catalytic activity compared to noble metal (Au, Ag, Pt, Pd) based catalysts [2]. HEA/Graphene (HEA:G) composites with varied weight percentage ratios of HEA and graphene have shown remarkable catalytic behavior towards water oxidation and non-enzymatic urea detection [3-4]. This response is due to the synergistic effect of HEA in catalyzing the redox reaction and graphene in accelerating the electron transfer process. Hence HEA based composites can replace traditional metal-based catalysts and can bring a great revolution in energy storage and sensing applications. This work illustrates the electro-catalytic behavior of HEA:G towards enzyme-less oxidation of glucose.

The mechanical milling of metal (70 wt %) powders (nickel, copper, iron, cobalt, chromium) and high purity graphite (30 wt %) was carried out for 100 h followed by sonication assisted exfoliation to produce HEA:G (70:30) composite. As produced composite was subjected to microscopic and spectroscopic studies for structural analysis. The electrochemical characterization was performed using potentiostat Biologic via cyclic voltammetry (CV) and differential voltammetry (DPV) techniques to study the sensing ability of HEA:G composites towards glucose detection in PBS as supporting electrolyte.

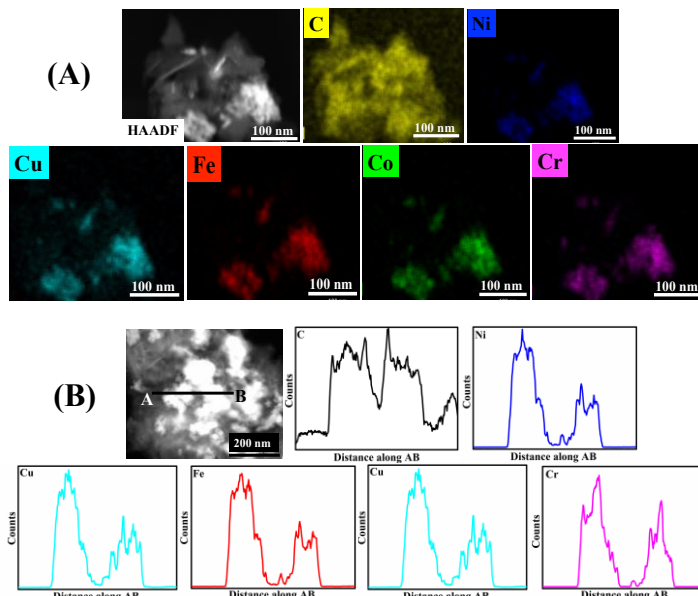
Fig. 1A, 1B and 1C represent XRD profile, AFM image and high-resolution TEM image respectively of the as-synthesized HEA:G composite. In the XRD patterns, the FCC peaks indicate the formation of solid solution multi-metal (NiCuFeCoCr) alloy nanoparticle integrated with a hexagonal graphitic phase (peak corresponding to  $2\theta = 42.5^\circ$  (010)). The average crystalline size of HEA nanoparticles calculated using the Debye Scherrer formula was found to be 8 nm. The distribution of HEA nanoparticles on a few-layered graphene sheet is evident from the representative AFM and TEM images. STEM-EDS technique was used to obtain compositional and line profile scans from the HEA:G composite as indicated in Fig. 2A and 2B. The compositional line scans clearly indicate the co-presence of all the five component metals (Ni, Cu, Fe, Co, Cr) on graphene (C) sheets forming multi-component alloy nanostructure (HEA) on graphene.

The catalytic ability of the HEA:G composite was investigated for the detection of glucose in PBS. The CV responses against 50 mM glucose at different scan rate and at different concentrations of glucose showed that, the oxidation current increase linearly with increase in the scan rate and glucose concentration indicating that the process is diffusional controlled thermodynamically. Fig. 3A represents the DPV response against different concentrations of glucose (1 mM to 50 mM) indicating the oxidation of glucose at 0.45 V with a corresponding linear increase in the oxidation currents. Fig. 3B represent the linear regression plots wherein the slopes corresponds to the sensitivity of the HEA:G composite. The

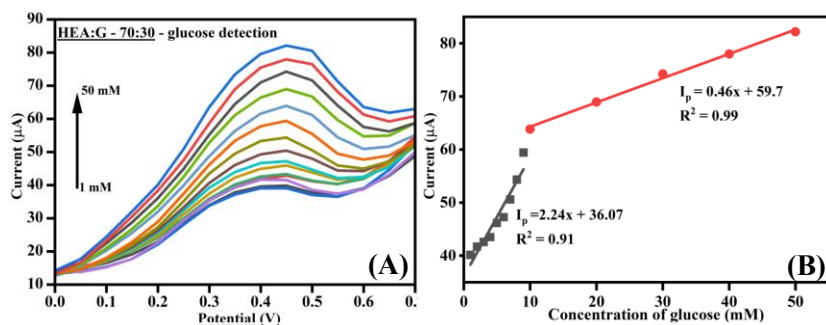
sensitivity was found to be 2.24  $\mu\text{A}/\text{mM}$  and 0.46  $\mu\text{A}/\text{mM}$  with wide linearity. Hence, HEA:G composites can be used to fabricate efficient non-enzymatic electrochemical sensors.



**Figure 1.** (A)XRD pattern (B)AFM topographical image (C)TEM bright field image of HEA:G composite



**Figure 2.** Representative of HAADF – TEM (A) - compositional mapping and (B) - line profiles obtained for HEA-G composite – 70:30 confirming the presence of constituents (Co, Cr, Cu, Fe, Ni) of HEA nanoparticle on graphene (C).



**Figure 3.** (A) DPV response at different concentrations of glucose. (B) Linear plot representing sensitivity of HEA:G composite

**References:**

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 [3] Nandan et al., Chem.commun **57** (2021) p. 611.  
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