

## An investigation on anti-corrosion properties of electroplated copper-graphene nano-composites

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### Abstract

In this report, graphene sheets have been synthesized by electrochemical intercalation and exfoliation process. The (001) and (002) plane of graphene sheets at a  $2\theta$  angle of 13.2 and 26.13 confirmed by X-ray diffraction pattern. (001) plane shows graphene oxide present in prepared graphene sheets. Transparent like layer confirmed from transmission electron microscope (TEM). High-resolution TEM confirms 8-12 layers present in graphene sheets. The as-received graphene sheets have been used as reinforcement with copper matrix to synthesize Cu-Gr nanocomposite by electrodeposition method. The results and investigations of Cu-Gr composite thin films deposited from the bath containing 0.1g/L and 0.5g/L graphene concentrations with acidic copper sulfate solution have been compared. The surface morphology and roughness of composites were studied by SEM, AFM and surface profiler. The presence of graphene in Cu-Gr nanocomposite confirmed by EDS analysis. It was observed that the reinforcement particle has increased the mechanical properties of Cu-Gr composite with the addition of copper matrix. The hardness of 0.5g/L Cu-Gr composite shows 30% higher hardness as compared to copper thin film. The corrosion resistance of sample was studied by a voltammetric method in standard borate buffer solution. The corrosion properties like Tafel constants and corrosion potential and currents were extracted and analyzed. For nano-composites of 0.5g/L graphene % the values are,  $\beta_a=177.37$  mv,  $\beta_c=138.51$  mv,  $I_{corr} = 9.3165 \times 10^{-7}$  Amp/cm<sup>2</sup>,  $E_{corr} = -0.051$  volts and corrosion rate 0.01028 mm/a as comparison to the corrosion rate of pure electroplated copper of a value of 0.029 mm/a. The corrosion rate of 0.5g/L Cu-Gr composite was found to be decreased by 2.7 times as compared to pure copper thin films. The structure of the films before and after corrosion was also analyzed to co-relate the electrochemical and structural relationship.

**Keywords:** Graphene; Electrochemical; TEM; Nanocomposite; copper.

### Introduction

Corrosion of materials is a major problem, which affects industries and human life. Corrosion protection of material increases the life of the material and decreases cost. Researchers have used various corrosion protection techniques to decrease the corrosion rate. Recently graphene and graphene-based nanocomposite coatings have shown to increase the life of materials. Graphene sheets coated on Cu, Ni and metal-graphene composite coatings of Cu-Cr, Gr-Ni, and Cu-Gr have been used for corrosion protection[1–6].

The copper materials and its alloys find huge applications and are being used in various sectors due to their impressive electrical and thermal conductivity. These are used for seawater applications for their corrosion resistance and antifouling properties. The graphene sheets added into copper matrix to prepare Cu-Gr composite, give higher corrosion resistance as compared to pure copper material[7,8].

Graphene is a two dimensional one layer material with  $sp^2$ -bonded carbon atoms arranged in hexagonal crystal lattice structure. Graphene has been demanded in many areas of science and technology due to its higher physical and chemical properties, involving strong mechanical strength and excellent electrical and thermal conductivity[9,10].

In the present work, graphene sheets have been synthesized by electrochemical exfoliation process. The prepared graphene sheets introduced as reinforcement with copper matrix to prepare Cu-Gr composite by electrodeposition route[11]. The analysis of corrosion behavior of prepared copper and Cu-Gr coating samples was carried out in standard borate buffer solution.

## **2. Experimental**

### **2.1. Synthesis of Graphene**

The graphene sheets were synthesized by electrochemical exfoliation route. A graphite sheet used as a counter electrode and another graphite sheet of exposed area  $0.45 \text{ cm}^2$  was used as working electrode while the  $1 \text{ M HNO}_3$  solution was used as an electrolyte. At first, a cathodic pretreatment was supplied to working electrode at a DC potential of  $3 \text{ V}$  for 10 minutes and after that  $10 \text{ V}$  for 10 s applied to the working electrode. The cathodic pre-treated working electrode connected as anode and other graphite sheet was connected as a cathode to a DC source for anodic treatment. A voltage range of  $0\text{-}8 \text{ V}$  was applied to the working electrode through a gradual increase of  $0.5 \text{ V}$  per 3 min. After exfoliation, the dispersed graphene electrolyte was washed thoroughly to remove acidic particles. The purified graphene sheets dispersed with distilled water by ultra-sonication.

### **2.2. Electrodeposition**

The copper and Cu-graphene composite coatings were deposited on a polished steel substrate. A graphite sheet was used as anode and steel substrate (area  $500 \text{ mm}^2$ ) as a cathode in the acidic electrolyte of  $1 \text{ M CuSO}_4 \cdot 5 \text{ H}_2\text{O}$  with various graphene concentrations of  $0.1 \text{ g/L}$  and  $0.5 \text{ g/L}$ , The pH of the electrolyte was maintained 1 by adding  $\text{H}_2\text{SO}_4$ . The electrodeposition of films carried out at a temperature of  $15\text{-}17^\circ$  and up to 20 min with a DC supply of  $2 \text{ V}$  in presence of sonication environment. A surfactant like SDS was added with the electrolyte to reduce agglomeration of graphene material during electrodeposition of Cu-Gr composite.

### **2.3. Electrochemical corrosion testing and characterization**

The synthesized graphene sheets were characterized using Ultima IV system X-ray diffractometer for X-ray diffraction study with  $\text{Cu K}_\alpha$  X-ray source for both graphene and Cu-Gr composite films. Functional groups of graphene sheets were analyzed by FTIR spectra. Field Emission Scanning Electron Microscope (FESEM) was used to obtain morphology of graphene sheets, Transmission electron microscope (TEM) and High-resolution Transmission electron microscope (HRTEM) were used for layer structure study of graphene. Topography and elemental analysis was done with the help of Scanning electron microscopy (SEM, JEOL JSM 6480 LV) combined with EDS (energy-dispersion spectrometer). An electrochemical workstation (Core studio5) was used to investigate the electrochemical corrosion behavior of prepared coated samples. The Potentiodynamic polarization tests were performed with standard borate buffer electrolyte. A standard three-electrode cell of electrochemical set-up consisting of exposed area  $0.6 \text{ mm}^2$  was used as working electrode, platinum foil as the counter electrode and saturated calomel electrode (SCE) as the reference electrode.

### 3. Results and discussion

#### 3.1. Physicochemical properties of as-synthesised graphene

The prepared graphene sheets were synthesized successfully by electrochemical exfoliation process for the fabrication of Cu-Gr composite. Fig 1. shows the structural and morphological structure of prepared graphene sheets. The dispersion of graphene sheets indicated by black colour shows stable dispersion of graphene with double distilled water. Fig. 1(a) depicts the XRD pattern of as-synthesized graphene sheets. A small peak centered at  $2\theta=13.2^\circ$  was ascribed to the (001) plane which indicates small amount of GO present in prepared graphene sheets which was due to the presence of oxygen functional groups in graphene sheets. A sharp peak centered at  $2\theta=26.13^\circ$  corresponding to (002) plane with d spacing of  $\approx 0.72\text{nm}$  signature of crystal graphene was seen. Fig. 1(b) showing FTIR spectra of as-synthesized graphene sheets confirmed the presence of elemental and functional groups. The stretching vibration of carbon/oxygen bonds(C=O), the vibration of carboxyl(C-OH). epoxide(C-O-C) and aloxide(C-O) groups present was observed in IR radiations of 1710,1385,1226, and 1034  $\text{cm}^{-1}$  respectively. The elemental functional groups confirm the presence of oxygen functional groups present in graphene sheets. The C=C stretching vibration of carbon bond at  $1585\text{cm}^{-1}$  confirms the aromaticity of graphene structure in as-synthesized graphene sheets. Fig.1(c) shows the UV-Vis spectrum of prepared graphene and the spectrum at 262 nm and a 300nm peak attributed to  $\pi-\pi^*$  transition of aromatic C-C bonds and  $n-\pi^*$  transition of C=O bonds respectively. Fig 1(d), (e) and (f) shows the FESEM, TEM and HRTEM image of graphene sheets respectively. The FESEM image shows the layer and folded structure of graphene sheets. TEM analysis shows the partial transparency like structure of graphene sheets. HRTEM shows 8-10 layer structure present in as-synthesised graphene sheets.

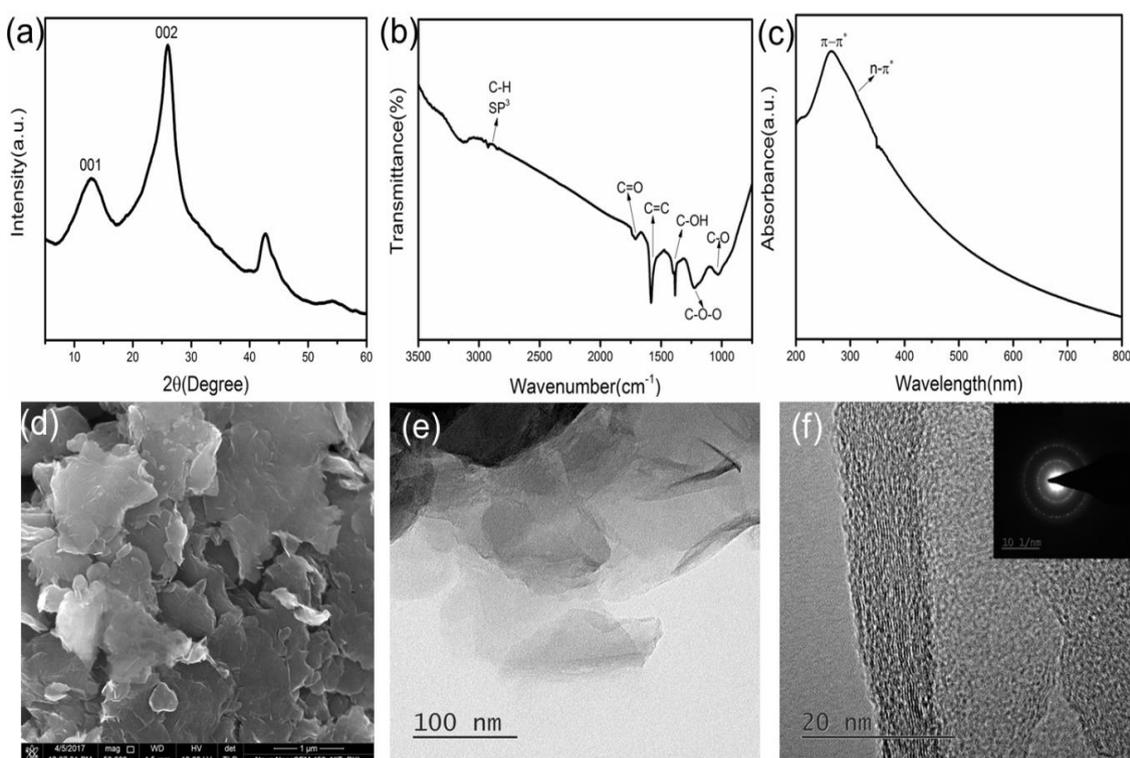


Fig. 1 (a) XRD pattern, (b) FTIR spectra, (c) UV-Vis spectra, (d) FESEM, (e) TEM and (f) HRTEM of graphene sheets

#### 3.2. Morphology and microstructure of coating samples

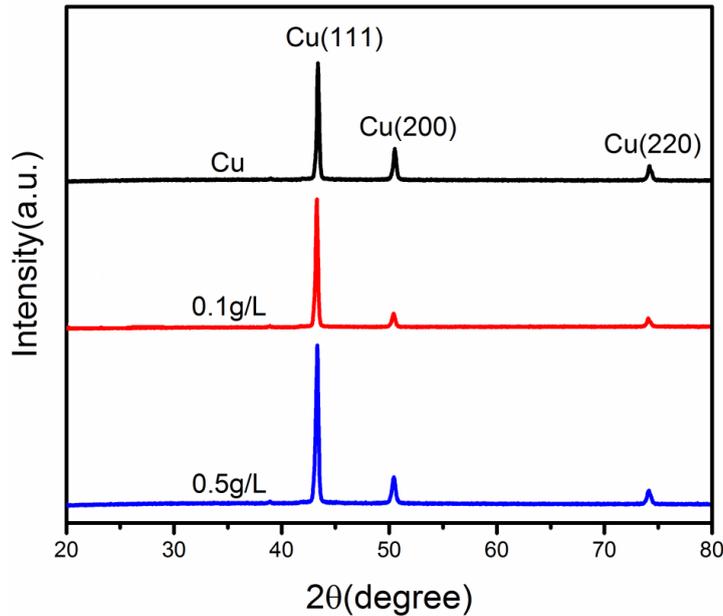


Fig.2. XRD pattern of copper and Cu-Gr composite coatings

Fig.2 shows the XRD pattern of prepared coating samples with graphene concentration of 0.1g/L and 0.5g/L. In XRD pattern we observed that with an increase in graphene sheets with copper matrix the intensity and FWHM of composite increased. The intensity of copper index (111) at  $2\theta=43.43^\circ$  increased with increase in graphene concentration whereas the intensity of the copper peak at  $2\theta=50.70^\circ$  of the index (200) decreased. There was no graphene peak present in Cu-Gr XRD pattern due to a small amount of graphene added into the copper matrix. The presence of graphene was confirmed by EDS spectra. Fig 3.(a),(c) and (e) shows the SEM image of 0 g/L Gr, 0.1g/L Gr and 0.5g/L Gr graphene concentration with copper matrix. The grains in Cu-Gr composite was found to be more compacted than that of copper thin films. The presence of graphene cannot be seen by topographybut it was confirmed by EDS analysis. The EDS spectra were analyzed over the entire selected area of SEM image of copper and Cu-Gr coating and it showed carbon peak(C) and copper peak (Cu) in Cu-Gr composite and only Cu peak in copper thin films. The carbon peak confirms the presence of graphene in Cu-Gr composite.

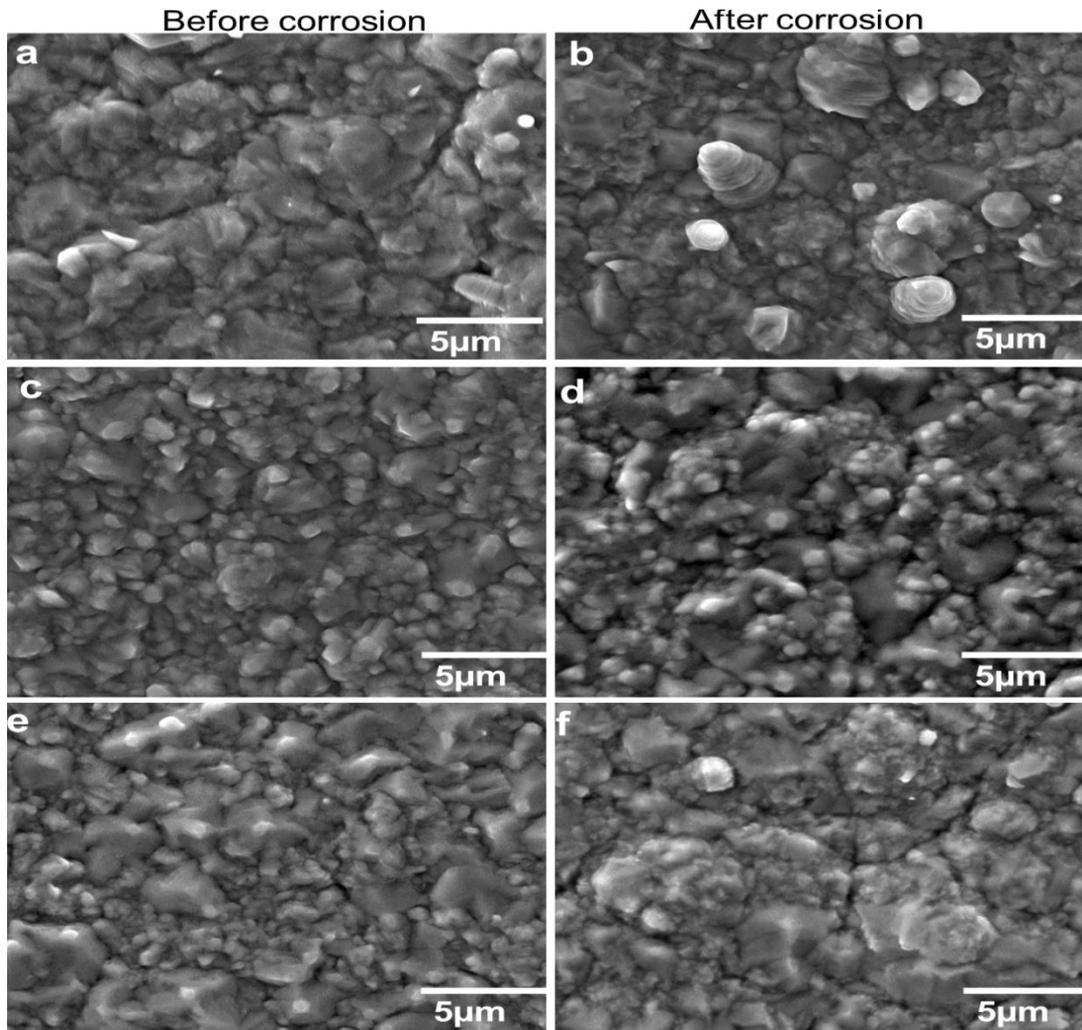


Fig.2. SEM image of Cu

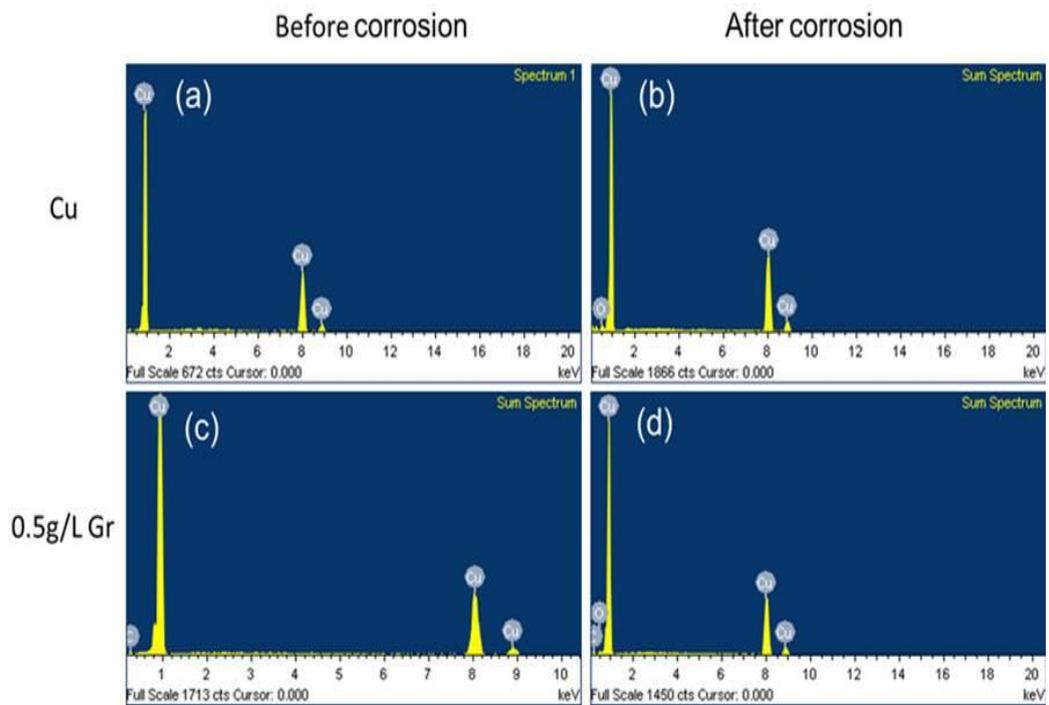
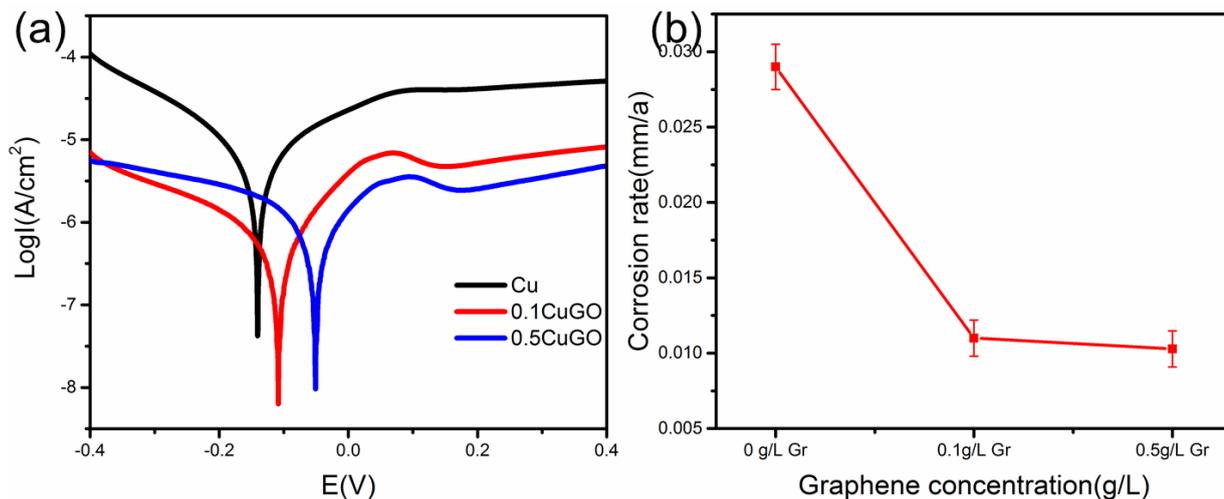


Fig.3. EDS spectra of Cu and 0.5Cu-Gr coating samples before and after corrosion

### 3.3. Electrochemical corrosion behavior of coatings

Fig.4. shows the potential dynamic polarization curve of copper and Cu-Gr coating samples performed in standard borate buffer electrolyte. The samples have been tested at a potential of -4V to +4V with a scan rate of 5mV/S versus open circuit potential (OCP). From the polarization curve corrosion potential shifted positively with an increase in graphene concentration. The corrosion potential of Cu shows -0.189 as compared to 0.1g/L Gr and 0.5g/L Gr of -0.16 and -0.06 respectively. The corrosion rate of Cu, 0.1g/L gr and 0.5g/L Gr composite shows 0.029,0.017 and 0.0128mm/a respectively. The corrosion rate decreases with increase in graphene concentration. The corrosion rate of 0.5g/L Cu-Gr composite decreases up to 2.7 times as compared to pure copper thin film. Fig.2 (b), (d) and (f) shows the SEM analysis of Cu and Cu-Gr composites. After corrosion analysis some white particles were seen on Cu thin films. These small white particles were more prominent in 0.1g/L Cu-Gr composite than that of 0.5g/L Cu-Gr composite due to the presence of graphene sheets. The intensity of (111) plane index affects the corrosion properties of the composite. Fig.3 (b) and (d) shows EDS analysis of Cu and 0.5g/L Cu-gr composite and we can say some oxide particles were present on samples after corrosion.



### Conclusion

Graphene sheets have been synthesized successfully by electrochemical exfoliation process. (001) plane and (002) planes of graphene sheet confirm the GO peak and crystal structure of graphene. FTIR spectra confirm the oxygen functional groups present in the graphene sheets. Graphene sheets were added into copper matrix to synthesize Cu-Gr composite. The Cu and Cu-Gr films were successfully coated on a steel substrate. The presence of graphene in Cu-Gr composite was confirmed by EDS analysis. Graphene sheets in Cu-Gr composite changed its morphology due to fine grain size deposited and hence by reducing the grain size of Cu-Gr composite. The Electrochemical corrosion studies were conducted on Cu and Cu-Gr composite in borate buffer solution and it showed 2.7 times higher corrosion resistance of composite in comparison to the bare copper coating.

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