# Electrochemically functionalized graphene as an anti-corrosion reinforcement in Cu matrix composite thin films

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## Abstract

In this article, Cu-Gr composite thin films are prepared by electrodeposition route using in-house synthesized graphene sheets. Graphene sheets are synthesized by electrochemical exfoliation route using 1M $HClO_4$ acid as electrolyte. Graphene sheets have been confirmed by XRD, FTIR, FESEM and TEM microscopy. The (002) plane of graphene sheets are observed at $2\theta$ of 25.66°. The (002) plane confirms the crystal structure of carbon peaks. The stretching vibration of C=C bond at a wavelength of 1577 $cm^{-1}$ and other functional groups of carboxyl and epoxide groups have been observed from FTIR. TEM microscopy confirms the transparent structure of graphene sheets. The prepared graphene sheets were used as reinforcement with a copper matrix to synthesis Cu-Gr composite. The graphene concentration of 0.1g/L and 0.3g/L was added with 1M $CuSO_4.5H_2O$ electrolyte. The prepared Cu-Gr nanocomposite thin films have been analyzed by XRD, SEM and EDS for morphological and analytical study. The presence of graphene sheets in Cu-Gr composite was confirmed by EDS analysis. The prepared Cu-Gr nanocomposite thin film shows 28% higher corrosion resistance as compared to pure copper thin films.

**Keywords:** Graphene, Nanocomposite, Electrodeposition, Copper.

## Introduction

Copper and its alloys are hugely demand in industry and research area due to its outstanding properties. It shows high electrical and thermal conductivity, mechanical workability and good corrosion resistance [1]. Copper is very frequently used in sheets and pipelines in electronic industries, power stations, cooling towers, heat exchangers and production of wires [2]. Therefore it is used as various electrical and thermal applications such as heat exchangers and electro friction materials. Copper metal shows good corrosion resistance in the atmosphere and other chemical environments. The corrosion property of copper decreases its life [3,4]. Therefore for corrosion protection, copper has attracted too much attention and various studies have been conducted to solve the problem. In this regard, researchers coated the copper surface and made copper alloys to reduce corrosion properties. In recent years researchers have used graphene as the protection material against corrosion of copper [5]. Graphene is a 2D material of $sp^2$-bonded carbon atoms arranged in hexagonal patterns. Graphene sheets have higher mechanical, electrical and thermal properties [6-8]. Graphene sheets are coated with Cu and Ni materials by the CVD method to get protection against corrosion [5,9]. However the graphene based coating has reasonable doubt over long-term protection and mechanical failure over long time use coated by CVD method [10]. Graphene sheets are added with copper matrix to produce a copper-graphene composite may give enhanced corrosion resistance. The composites also show enhanced physical and thermal properties as compared to copper thin films [11,12].

Recently, many researchers used graphene as reinforcement with copper matrix to improve physical and chemical properties of copper. Jian Wang et al. have synthesized Cu-Gr composite by an electric field-activated pressure-assisted synthesis (FAPAS) method [13]. They observed 0.5gm/L Gr concentration improves hardness of 17.6% (85HV) as compared to copper (70HV) and corrosion resistance of composite increases as compared to pure copper. Faisal Nazeer et al have reported copper reduced graphene oxide composite by powder metallurgy technique [14]. The hardness of Cu-RGO composite increases 61% (71.2HV) as compared to copper (44HV).

In the current investigation an attempt has been made to prepare Cu-Gr nanocomposite films by electrodeposition route with in-house synthesized graphene sheets. The graphene sheets are synthesized by electrochemical exfoliation route. The corrosion behavior of copper and Cu-Gr nanocomposite films is carried out by 3.5% NaCl solution[15].

## 2. Experimental

### 2.1 Synthesis of graphene sheets

Graphene sheets were synthesized through electrochemical exfoliation route by using graphite sheet. In this route, a graphite sheet was used as working electrode and another was used as counter electrode. The acidic solution of 1M $HClO_4$ with double distilled water was used as the electrolyte. At first, a cathodic pre-treatment was given to the working electrode to remove unwanted particles from the working electrode. After cathodic pre-treatment the working electrode was connected as the anode and a potential span of 1-8 volts with a scan rate of 0.5V per 3 minutes was applied. The graphene sheets intercalated and settled down at the bottom. The collected graphene sheets were washed thoroughly with distilled water. Then the graphene sheets were dispersed with distilled water by using ultra-sonication. The dispersed graphene sheets were dried at 80 °C and the graphene sheets were collected.

### 2.2 Electrodeposition of Copper and Cu-Gr nanocomposite

Copper and Cu-Gr thin films were electrochemically grown on a polished steel substrate. The steel substrate was connected as a cathode and a graphite sheet was connected as the anode in the electrodeposition system. The electrolyte of 1M $CuSO_4$ was used as a base solution and various graphene concentrations (0, 0.1, 0.5g/L) were added to synthesise Cu and Cu-Gr nanocomposite thin films. A DC current supply of 2V was applied to the electrodes. The experiment was completed at a temperature of 15 °C in 20 minutes. A polymeric surfactant (SDS 300ppm per 0.5g/L) was used to reduce the agglomeration of graphene sheets during electrodeposition. Then, the prepared films were subjected for further characterization.

### 2.3. Characterization and electrochemical corrosion testing

As prepared graphene sheet and thin films were analyzed using X-ray diffraction study (Ultima IV) with Cu Kα X-ray source. The functional groups of graphene sheets were analyzed by Fourier-transform infrared spectroscopy (FTIR). The morphology of graphene sheets was analyzed by Field Emission scanning electron (FESEM) and Transmission electron microscopy (TEM). The morphology of copper and Cu-Gr films were analyzed by scanning electron microscopy (SEM, JEOL JSM 6480 LV) and elemental analysis was done by an energy-dispersion spectrometer (EDS). The corrosion behavior of Cu and Cu-Gr films were studied by an electrochemical workstation (Core studio5). The potentio-dynamic polarization tests were carried out in 3.5% NaCl electrolyte. A standard three electrode system was connected to a $0.45cm^2$ area of Cu and Cu-Gr film acting as working electrode, a platinum rod being used as counter electrode and a saturated calomel electrode (SCE) as a reference electrode.

## 3. Results and discussion

### 3.1. Physicochemical properties of Graphene sheets

Graphene sheets were prepared by electrochemical exfoliation technique for the fabrication of Cu-Gr nanocomposites. Fig.1 shows the morphological and analytical study of graphene sheets. Fig.1 (a) shows the XRD pattern of graphene sheets. (002) the plane of d spacing ≈0.73nm, observed at

2θ=25.7°, gives the signature of crystal graphene. Fig. 1 (b) shows the FTIR spectra of graphene sheets which show the presence of elemental and oxygen functional groups. FTIR spectra observes transmittance peaks at 1711, 1386, 1227, 1029 and 625 $cm^{-1}$ of carbon/oxygen bonds, carboxyl(C-OH), epoxide(C-O-C), aloxide(C-O) and C-H bonds respectively. From these functional groups, we confirm the presence of oxygen in graphene sheets. The vibration of the C=C stretching bond observed at 1578 $cm^{-1}$ shows aromacity of graphene sheets. Fig 1(c) shows the FESEM image of graphene sheets. The image shows the crystal layer structure of graphene sheets. Fig 1(d) shows TEM image of the graphene sheet and it shows a semitransparent like layer of graphene sheets.

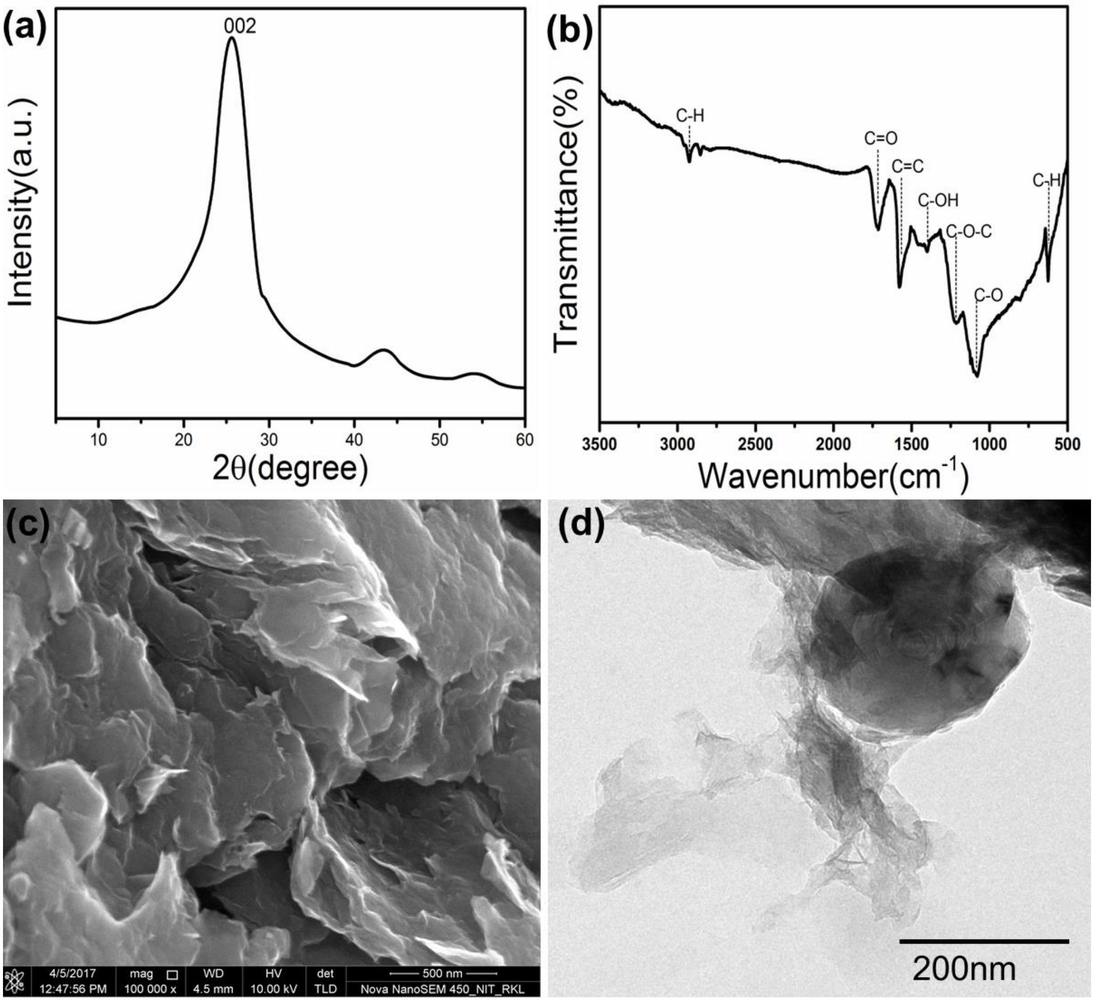


**Fig.1.** (a) XRD spectra (b) FTIR (c) FESEM and (d) TEM of graphene sheet.

**2.2 Morphology and microstructure of thin films**

Fig. 2(a) shows the X-ray diffractogram of Cu and Cu-Gr thin films. It shows the diffraction peaks at 2θ = 43.52°, 50.75° and 74.35° which can be indexed as (111), (200) and (220) respectively of prepared coated samples. The (220) plane of composite films decreases with increase in graphene concentration. Fig 2 shows the SEM image of copper and copper-Gr thin films (b) Cu, (c) 0.1Cu-Gr, (d) 0.3Cu-Gr and (e) EDS spectra of the 0.3Cu-Gr nanocomposite. The grain structure of thin films gets more compacted with an increase in graphene sheets. The grain structure was finer than pure copper thin films. The presence of graphene sheets was confirmed by the EDS spectra of 0.3g/L graphene concentration Cu-Gr composite. The carbon peak on EDS spectra confirms the presence of graphene in Cu-Gr composite.

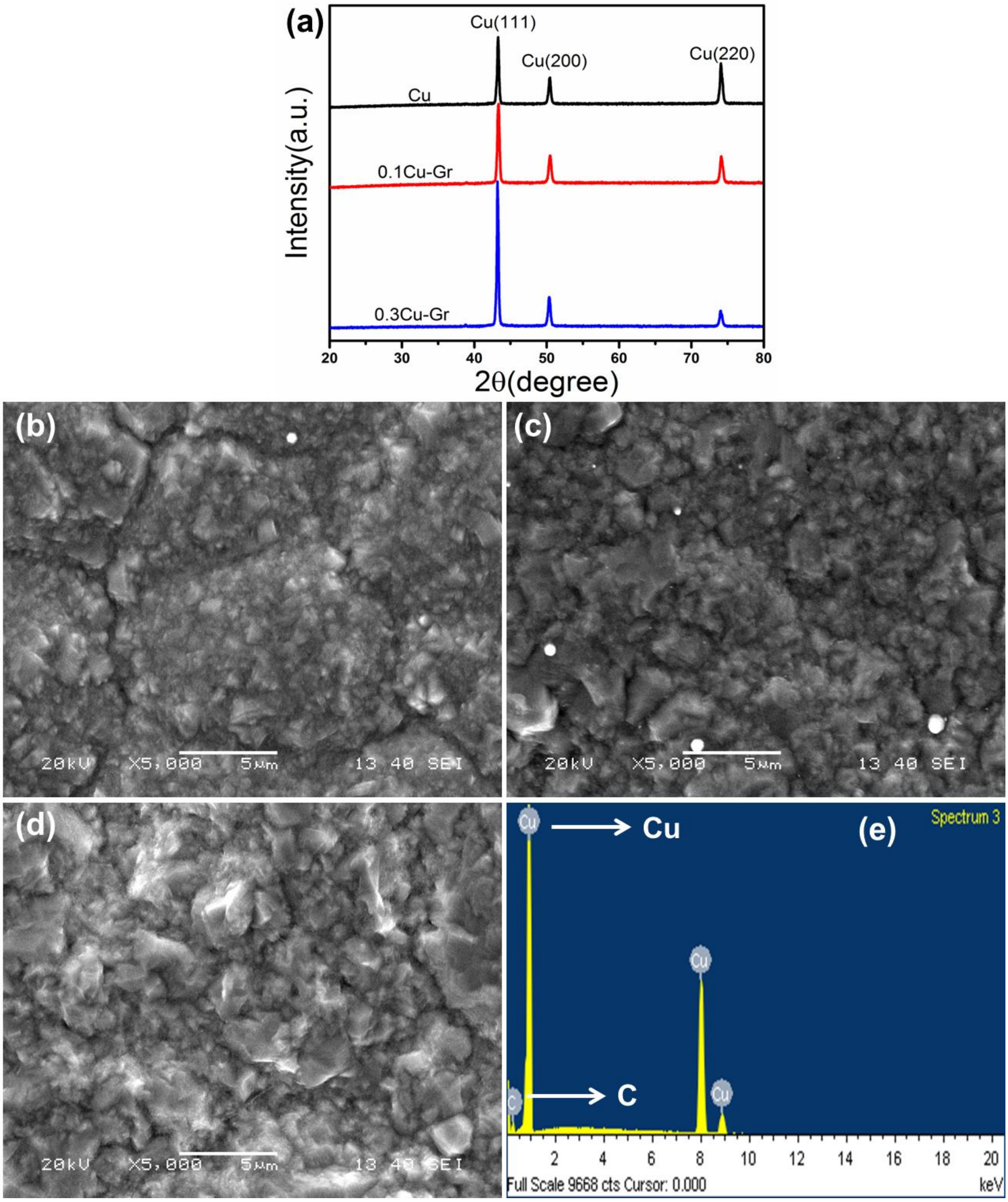


**Fig.2.** (a) XRD diffraction image of thin films and SEM image of (b) Cu (c) 0.1Cu-Gr (d) 0.3Cu-Gr and (e) EDS of 0.3g/L Cu-Gr nanocomposite thin films.

### 3.3. Electrochemical corrosion behavior of thin films

The electrochemical corrosion study of copper and Cu-Gr nanocomposite thin films has been analyzed by three electrode system in a potentiostat. The Tafel polarization studies have been carried out in a 3.5% NaCl electrolyte. The Tafel polarization tests were performed by the polarization of ± 200mV through the open circuit potential at a scan rate of 5mV/s. Fig. 3 shows the Tafel polarization curves of Cu and Cu-Gr films. The oxidation reactions of thin films with 3.5% NaCl solution are expressed as follows:

$$Cu - 2e^{-} = Cu^{2+} \quad (1)$$

$$Cu^{2+} + 2H_2O = Cu^{2+} + 2H_2O \quad (2)$$

The reduction reactions of thin film with 3.5% NaCl solutions are

$$2H_2O + O_2 + 4e^- = 4OH^- \quad (3)$$
$$Cu^{2+} + 2H_2O + 2Cl^- = CuCl_2.2H_2O \quad (4)$$

Equation 1 and 2 shows the oxidation reaction of thin films and equation 3 and 4 shows the mechanism of oxidation reaction with 3.5% NaCl solution. Table.1 shows the corrosion parameters of the corrosion tests. The pure copper thin film, 0.1Cu-Gr and 0.3Cu-Gr nanocomposite films have shown corrosion potential ($E_{corr}$) of -0.395V, -0.27V and -0.245V respectively. The corrosion potential of Cu-Gr composite has become nobler with an increase in graphene concentration. The corrosion current densities ($I_{corr}$) of copper, 0.1Cu-Gr and 0.3Cu-Gr films are $4.75\times10^{-6}$, $2.82\times10^{-6}$ and $2.24\times10^{-6}$ respectively. Reduction in current density with increase in graphene concentration was observed with increase in corrosion potential. The corrosion rate of copper film shows 0.035 mm/yr, 0.1Cu-Gr and 0.3Cu-Gr nanocomposite shows 0.0331 and 0.025 mm/yr respectively. The graphene concentration of 0.3g/L Cu-Gr composite shows 28% higher corrosion resistance as compared to pure copper thin film. The corrosion rate decreases with increase in graphene concentration. Fig. 4 shows SEM image of Cu and Cu-Gr thin films after corrosion. The surface morphology of exposure samples showed a significant change as compared to their as deposited samples.

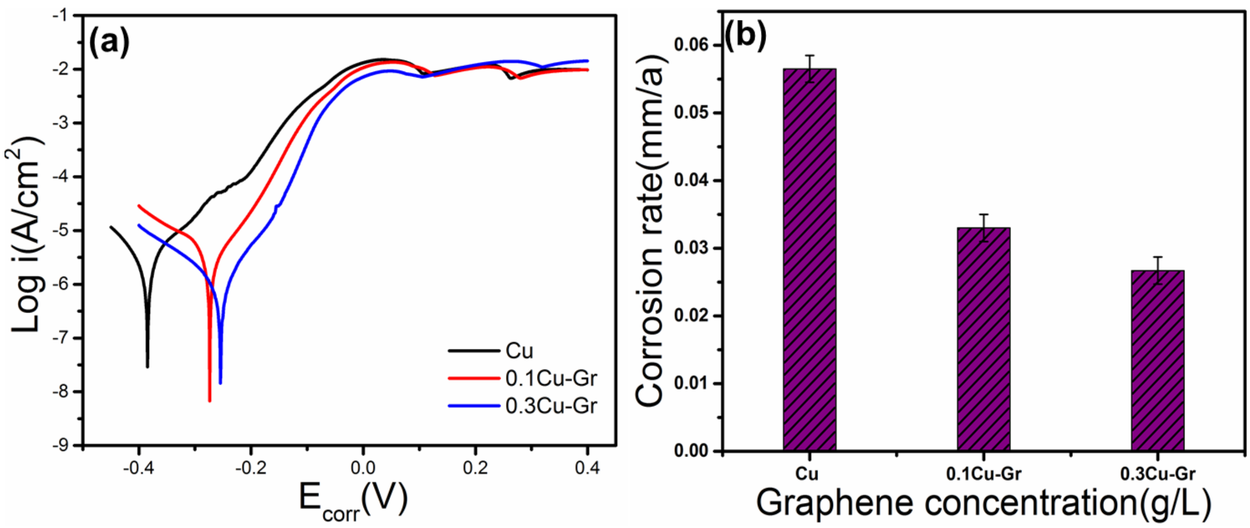


**Fig.3.** (a) Tafel polarization curves of Cu and Cu-Gr nanocomposite (b) Corrosion rate of thin films.

**Table 1.** Corrosion properties of Cu and Cu-Gr composite films.

| Sample | βa | βc | $I_0\times10^{-6}$ | $E_b$ | Corr rate(mm/a) |
|---|---|---|---|---|---|
| Cu | 100 | 131 | 2.86 | -0.3207 | 0.035 |
| 0.1Cu-Gr | 73.95 | 47 | 2.37 | -0.27 | 0.027 |
| 0.3Cu-Gr | 96.15 | 185.3 | 1.7 | -0.245 | 0.025 |

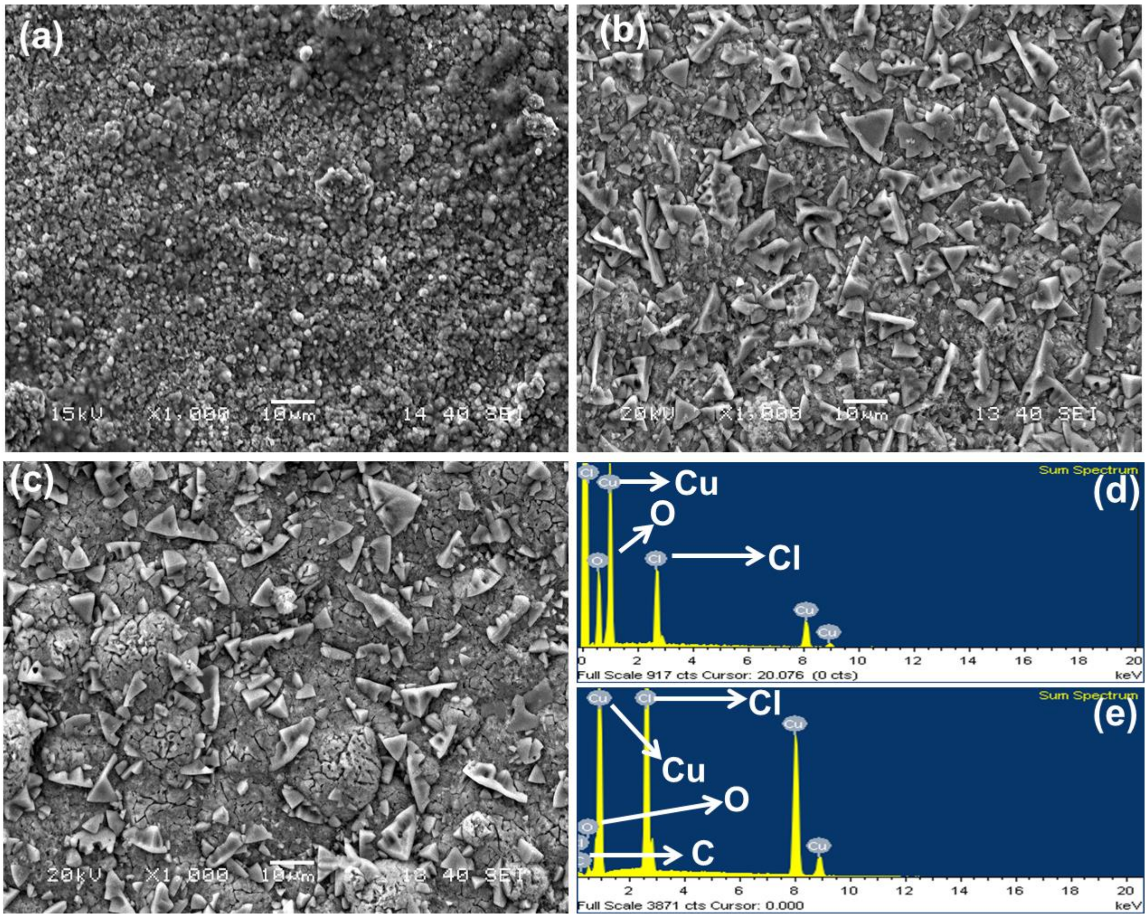


Fig. 4 SEM image of thin films after corrosion (a) Cu (b) 0.1Cu-Gr (c) 0.3Cu-Gr and (d) and (e) EDS of Cu and 0.3g/L Cu-Gr nanocomposite thin films after corrosion

## 4. Conclusion

Cu and Cu-Gr nanocomposite films have been successfully synthesized by electrodeposition route. In-house synthesized graphene sheets were used to prepare the Cu-Gr nanocomposite by electrochemical deposition. The morphology of Cu-Gr nanocomposite films were found to be compact with increase in graphene concentration as compared to copper thin film. The presence of graphene is also confirmed by EDS analysis. The corrosion rate of the copper film decreases with increase in graphene concentration. The corrosion rate of Cu-Gr nanocomposite shows 40% higher than copper films in 3.5% NaCl media.

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