

Sono-electroplating of Copper-Graphene nano-composite thin films for electrofriction applications

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ABSTRACT

Graphene has been used as a reinforcement material for improving the strength of metal matrix composite due to its outstanding mechanical properties. In the present paper, the copper-graphene nanocomposite films were synthesized onto the copper substrate by a simple and cost-effective electrodeposition process. The electrolyte contains CuSO_4 and H_2SO_4 with different concentrations of graphene (0.1, 0.3 and 0.5 g/L). The electrodeposition process was carried out at pH of 1 and at a temperature of 15-17 °C. Ultrasonication was used during electrodeposition for uniform dispersion of graphene with the copper matrix. The graphene sheets were synthesized by electrochemical exfoliation technique as nitric acid electrolyte. (001) and (002) planes of graphene sheets have been observed from X-ray diffraction. The aromatic ring of carbon C=C bond stretching vibration at 1580 cm^{-1} and oxygen functional groups have been observed from Fourier transform infrared spectroscopy spectra. The partial transparency and Few-layers (10-12) of graphene sheets have been observed by transmission electron microscope and High-resolution Transmission electron microscope. The SAED pattern shows the crystallographic and hexagonal structure of graphene sheets. The presences of Graphene in composite films were observed from elemental mapping analysis. There is a significant improvement of in the electrical conductivity of the films. The analysis of the wear properties of the films implies that the wear resistances has been increased with addition as well as increase of graphene content the films. The co-efficient of friction has also been decreased. However the study needs a critical assessment before drawing a definite conclusion.

Key Words: Graphene, Metal-matrix, Nano-composite, Thin Film, Electrodeposition, Sonication, Hardness, Resistivity, Wear

INTRODUCTION

Recent years copper-graphene nanocomposites have been investigated due to their outstanding mechanical and physical properties such as hardness, electrical and thermal properties. Therefore they are used as different electrical and thermal applications such as heat exchangers, electro friction materials, electrical brushes and high voltage applications. There are several methods to produce Cu-Graphene nano-composites such as powder metallurgy route, microwave assisted process, pulse electrodeposition and electrodeposition techniques for improving physical and chemical properties of Cu-graphene nano composite. Chokkakula et al. have reported a 96% increment in hardness and 30% higher in elastic modulus than the pure

copper films by pulse electrodeposition route. Himansu et al. have shown a 40% higher hardness and decrease electrical conductivity by pulse electrodeposition route. Gang hung et al. shows a 5% higher thermal conductivity, 17.2% young modulus and increased electrical conductivity as compared to copper thin film by electrodeposition route. K. Jagannadham et al. shows higher thermal conductivity (460 W/m.K) as compared to copper thermal conductivity (380 W/m.K) by electrodeposition route. From the above techniques electrodeposition or pulse electrodeposition was simple, fast and cost effective technique for nano-composite deposition. However there is always a concern on the distribution of the graphene sheets in the metal matrix, which can be achieved by adding an activation field to the depositing system. Coupling of ultrasound during electroplating can increase the deposition rate; henceforth can alter the physicochemical and other structural properties of the nano-composites to a great extent if one can manipulate the parameters optimally. Hence in this study copper-graphene nanocomposite films were prepared on a polished copper substrate by simple DC electrodeposition technique at low bath temperature in presence of ultrasound. Effects of graphene concentration with the copper matrix in composite films on the structure and physical properties have been studied by different analysis techniques.

EXPERIMENTAL PROCEDURE AND BRIEF FINDINGS

All the chemicals and solvents used were of analytical grade and have been used without further purification. High-grade pyrolytic graphite sheet of thickness 3 mm (Asbury Graphite Mills, IPG-15) was employed as both the working as well as counter electrodes in a voltage regulated DC bias system (Aplab, Model No. 7103). All experiments were conducted at the ambient condition of temperature and pressure, unless otherwise mentioned in the text. Copper films are electrodeposited on-to polished copper substrate of area 490 mm².

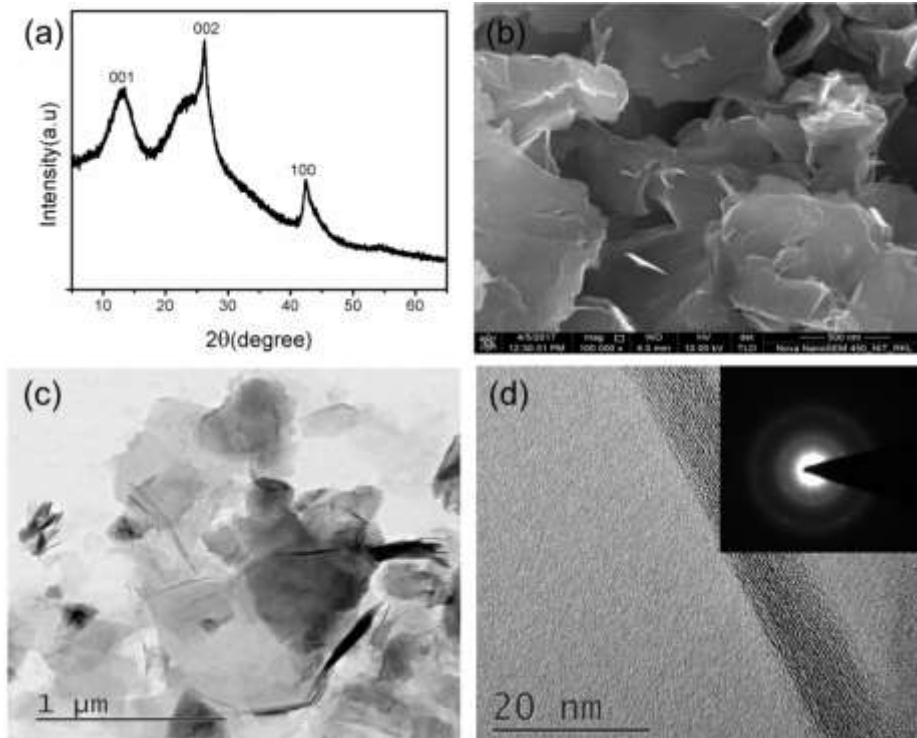


Fig.1 (a) XRD spectra (b) FESEM (c) TEM and (d) HRTEM image of in-house synthesized reduced graphene

Copper-Graphene composite foils are synthesized in an electrolytic bath consisting of 250 g/l copper sulphate and H₂SO₄ was added to maintain the pH~ 1. In order to avoid the agglomeration of Gr sheets in the electrolyte during the deposition, a polymeric surfactant like SDS (25 ppm for 0.5 g/L of Gr) was added. Graphene content dispersed in the electrolyte was varied between 0.1–0.5 g/L. However the optimum concentration was found to be 0.5 gm/L in

order to achieve Cu-Gr foils with high hardness, less agglomeration of Gr in matrix and good reproducibility. Bath temperature was maintained between 15–17°C. Electrodeposition was done with a two electrode system by using a DC power supply with an electrolytic Graphite sheet as anode and copper plate as cathode.

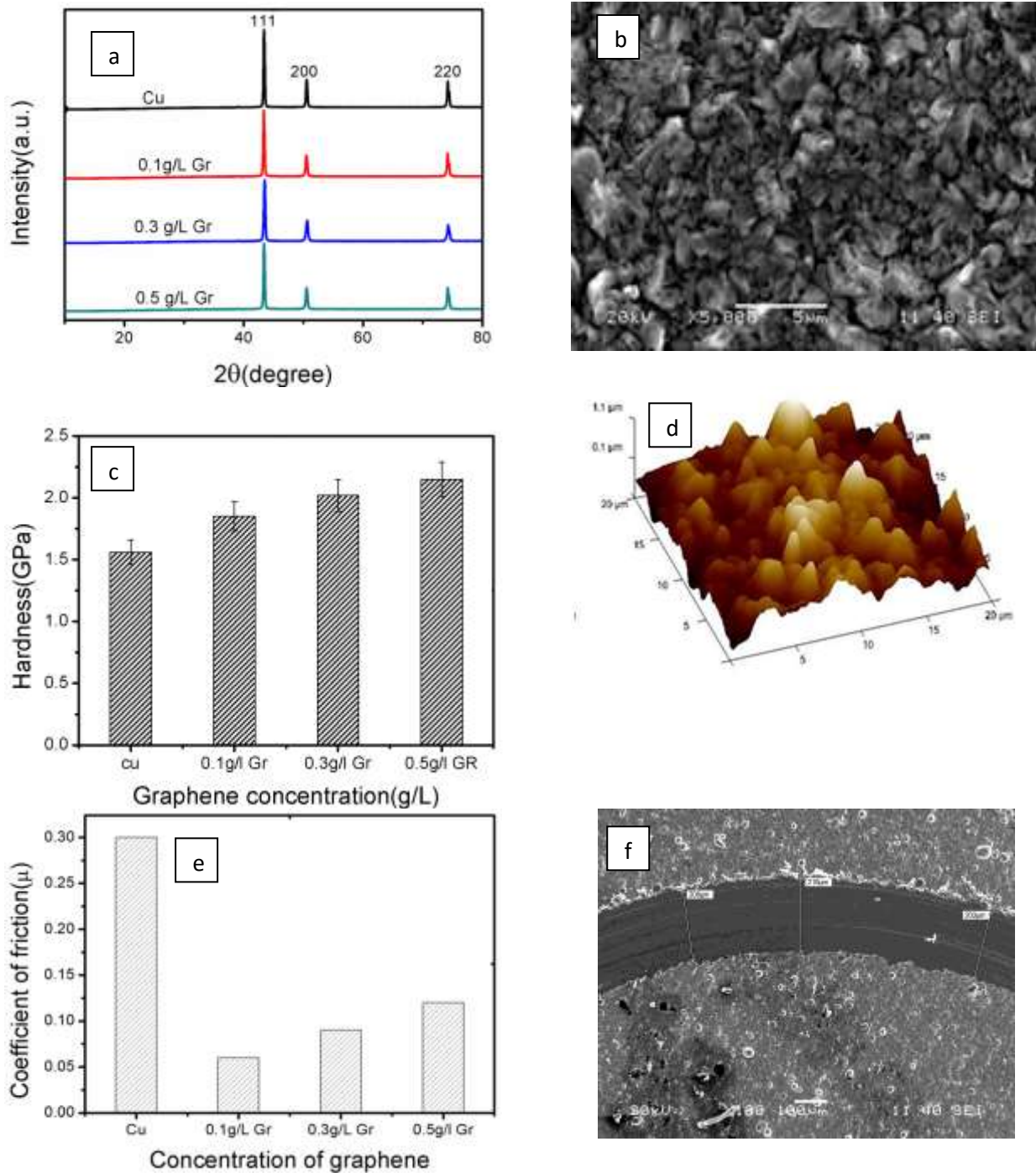


Fig 2: (a) XRD pattern at different graphene concentration, (b) SEM micrograph (0.5 g/l graphene), (c) variation of hardness with graphene concentration, (d) AFM image (0.5 g/l graphene), (e) variation of co-efficient of friction with graphene concentration and (f) SEM image of wear track (0.5 g/l graphene)of the synthesized Cu-graphene nano-composite thin films

Figure 1 represents the structure and morphological properties of prepared graphene sheets for the synthesis of the copper-graphene composite. Figure 1(a) shows the XRD pattern of graphene sheets. The XRD spectra show a sharp peak at 26.32° represents to the basal plane (002) and at 13.6° represents GO peak of (001) plane due to the oxygen functional groups. The layered graphene structure and hexagonal ring patterns can be confirmed by the morphological analysis. Figure 2 represents XRD pattern of Cu-graphene composite films in at different graphene concentrations in ultrasonic condition. The XRD peaks of the composites were conformed as pure Cu assigned by JCPDS (card no.040836) data. No graphene peak was observed as small amount of graphene was added in the electrolyte. But the presence of graphene was conformed from EDS characterization. The topography of composite films shows that by adding graphene particle, grain size has been increased. From elemental mapping the presence of graphene has been conformed in the Cu-graphene composite (Not shown here). Figure 2 also shows the 3D AFM images of the films on some selected areas of $(20 \times 20) \mu\text{m}^2$ from both the depositing conditions. The roughness of composite films have been observed from AFM analysis. The microhardness measurement of copper and Cu-graphene composites of different graphene concentration is also shown in the figure which confirms an improvement in the values. In ultrasonic condition hardness has increased as compared to silent condition due to the uniform distribution of graphene particles in copper matrix. The uniform dispersion of Gr in copper matrix might have arrested the grain growth and block the dislocation motion during deposition. The wear surface of the composite films is presented in the figure, which signifies an increase in wear resistance with addition of graphene to the pure Cu matrix. The electrical conductivity was also found to be increased. Resistivity of composites are decreased as compared to pure copper thinfilms due to the absence presence of oxide functional groups in graphene sheets.

CONCLUSIONS

The reduced graphene oxide (RGO) sheets were produced from in-house synthesized graphene by chemical route applying different reducing agents. The nano-composites were synthesized at low bath temperature. The EDS analysis shows the presence and variation of graphene content in the composite. The prepared composite shows 37% higher hardness as compared to pure copper thin films. Electrical resistivity of the composite has been decreased and wear resistance has been increased with addition of graphene to the copper matrix.

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