Stable copper nanowire-graphene oxide thin films for nonlinear photonics

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Abstract: Solution-based copper nanowire-graphene oxides are promising building blocks in future optoelectronics ranging from transparent electrodes to electrochromic displays to stretchable electronics. In this paper, a detailed study of the optical properties extending to non-linear properties is demonstrated. An enhancement of 43% is observed for the nonlinear optical properties of these thin films in comparison to a graphene oxide thin film. Moreover, its application as transparent conductive electrodes with 93% of the optical transmittance and a sheet resistance of 10 Ω/sq is manifested.

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1. Introduction

Low-dimensional materials attain much attention in the recent time due to the requirements of next-generation on-chip lightweight wearable, portable and flexible technologies [1,2]. For example, the transparent conductive electrodes (TCEs) are essential for optoelectronics like solar cells and displays [3]. In similar aspects, the nonlinear optical (NLO) properties of the materials can open a new platform for the optical technologies [4]. This kind of new optical materials considers a trade-off between cost-effectiveness, optical transmittance, refractive index, and electrical conductivity [5].

However, the performance limitation of these materials like zero bandgaps and low carrier mobilities lead to the development of mixed-dimensional or hybrid nanomaterials which form heterogeneous systems [6]. This kind of systems become a new attraction since it can overcome the traditional issues of lattice mismatch which are commonly observed in the multilayer bulk material structures [7] and open a new path for the next generation devices.

These structures interact through the dangling bond free van der Waal forces which results in varying functionalities and open a new platform for the extensive range of tunable applications like memristors and photodetectors [8,9]. However, understanding the stoichiometry of these structures remains a challenge. Materials like transitional metal dichalcogenides (TMDs), graphene, carbon nanotubes, quantum dots, and nanowires are commonly used for these studies [10–12].

Among those materials, graphene oxides (GOs) in the reduced form (rGOs) [13] is a widely used pseudo-two-dimensional cost-effective alternative for graphene. On the contrary to the graphene, we can tune the physical properties of GOs to create the bandgaps [14] with the controlled reduction process and is highly useful in optical [15–17], electrical [18,19] and energy storage applications [20,21]. The reduction results in the removal of oxygen groups from the atomic structure of GOs using different methods like thermal, chemical and photoreduction [22]. Alternatively, different nanomaterials like TiO₂, ZnO, gold, and silver are added to enhance and tune the properties of the GOs [23–25].

Copper nanowires (CuNWs), on the other hand, are cheaper compared to other metallic nanowires having absorption in the visible region like silver or gold, which are much in demand
in the field of transparent conductive electrodes (TCEs) [26] and electronics [27]. However, the oxidative nature of the copper material [28] is a significant hindrance to the application aspects of TCEs made of these nanowires. The issue is currently addressed with the passive protective coating around the CuNWs like core-shell structures [29] as well as plasmonic laser welding [30].

The heterogeneous system using rGOs [31] and graphene [32] with CuNWs are other methods widely used for the oxidation protective coating. Furthermore, these studies could not provide a detailed understanding of the interaction in the thin films. Besides, graphene material is limited by the absence of bandgap [33] which restricts its usage in the real applications.

Here we propose a stable oxidation resistant heterogeneous cost-effective CuNW-GO thin film (Fig. 1). In this paper, the primary focus is given to understand the influence of CuNWs in the controlled tuning of the intrinsic properties of the GOs. The studies are extended to understand the linear and nonlinear optical properties of these thin films which are not covered by other related literature. Further, it is demonstrated that the heterogeneous system has various applications like stable TCEs under extreme conditions.

![Fig. 1. Conceptual illustration of CuNW-GO thin film and energy transfer between CuNWs and GOs in the thin film where excited electrons from CuNWs results in the saturable absorption (SA) in the GOs (inserted).](image)

2. Methods

2.1. Fabrication methods

The following methodology was considered for the fabrication of CuNW-GO thin films. Graphene oxide (2 mg/ml) solution made using Hummers method [34] was obtained from the Sigma Aldrich and diluted to 0.03 mg/ml in water. CuNWs was prepared as a concentrated 2.2 ml ink as specified in our previous publication [27]. This ink was diluted with ethanol to achieve a concentration of 0.8 mg/ml, which makes the solution ideal for spraying and rapid drying on the substrate. CuNWs was spray coated on the plasma treated (to induce hydrophilicity and enable maximum adhesion of CuNWs) glass substrate at specific concentrations. It was then gently washed with glacial acetic acid to remove the HPC (Hydroxypropyl cellulose) and any oxides on the CuNWs. The coated glass substrate was then dried in a stream of nitrogen gas to ensure complete removal of the acetic acid and GO solution in specific concentrations resulting in CuNW-GO thin films. The final thickness of the resultant thin film is $\sim 1.6 \mu m$.

2.2. Characterization methods

A detailed understanding of the obtained CuNW-GO thin films was conducted using morphological, optical and electrical methods. The morphology of the thin films was studied using scanning electron microscopy (SEM) (Philips XL30) and atomic force microscopy (AFM) (Brucker).
The optical studies like absorption (Schimadzu), Raman (Renishaw), FTIR (Perkin-Elmer), UV-Visible (CARRY) measurements and surface plasmon enhancement (SPR) were performed on CuNW-GO thin films at ambient room conditions. 355 nm and 532 nm lasers were used to measure the photoluminescence and Raman spectrum respectively of the thin films. The photoluminescence (PL) studies were measured using a custom-built setup and a wavelength of 800 nm. A neutral filter is used to attain an attenuation of 1000 times. The detection of the luminescence intensity was measured using a photodetector (Thorlabs). SPR studies of thin films were conducted using the commercial Lumerical software with the central wavelengths of 532 and 790 nm. Here we considered a periodic array of CuNW structures instead of random nanowires to understand the nanowire shape giving highest SPR with the GO thin film coatings. A simulation unit was defined with a periodic unit cell having dimensions of $\lambda/40$ nm. Z-scan measurements were performed for the non-linear studies of the thin films using a custom-built setup with a femtosecond laser beam centered at wavelength 800 nm and a pulse duration of $\sim$100 fs using an objective of the 0.35x magnification and repetition rate of 10 kHz. The laser beam diameter was around 30 $\mu$m. A neutral density filter was employed to vary the input laser fluence continuously. The sample was mounted on a translation stage which moved along the z-axis concerning the focus of the lens. During the sample movement was closer to focus; the laser intensity would be higher leading to a self-focusing behavior in the sample leading to the variation of laser beam power as a function of z-position passing through the adjustable aperture in front of the power meter. The sheet resistance of the thin films was measured using the four-probe method (JANDEL 1000). The aging tests were performed using a preset micro oven (Labec) at a temperature of 80°C and a humidity of 85%. Zeta-potential measurements were conducted using KCL electrolyte in water solvent using SuRPass potentiostat.

3. Results and discussions

3.1. CuNW-GO thin film

Figure 1 shows the conceptual illustration of the energy transfer between CuNWs and GOs which results in a saturable absorption (SA) in GOs and oxidation resistance to the CuNWs. It can be seen that CuNW-GO thin films exhibit distinct properties as shown in Fig. 2. The scanning electron microscopy (SEM) image of the thin film reveals a uniform coverage of GO films on the CuNW distribution (Fig. 2(a)). The average thickness of the thin films with different concentrations is around 1.6 $\mu$m (Fig. 2(b)). The average roughness of the obtained CuNW-GO thin film is measured using atomic force microscopy (AFM) and is about 9.4 nm (Fig. 2(c)).

The coverage density of different concentrations of CuNWs in thin films is given in Fig. 2(d) and can be considered to have around 30 to 40 nanowires per cm$^2$. The CuNW distribution has an average diameter of 60 nm, length 100 $\mu$m and roughness of 103 nm (Fig. 2(e)). GO flakes have an average flake size of 5 $\mu$m with an average roughness of 36 nm (Fig. 2(f)). Zeta potential, $\zeta_p$ measurements are conducted to understand the surface charges of the thin film. It is observed that a high surface charge of 62 eV for GOs, and with the addition of CuNWs, the surface charge of GOs is increased to 73 eV. These results have been clear evidence of negative surface charge for these films.

3.2. Optical properties of CuNW-GO thin film

GO atomic structure consists of several oxidative groups like carboxyl (C-O), hydroxyl (OH) and epoxy which results in the formation of a mixture of $sp^2$ and $sp^3$ carbon atom ratios in the material where $sp^2$ carbon atoms bind with nearby carbon atoms and $sp^3$ carbon atoms bind with nearby oxygen-containing functional groups. The Fourier transform infrared spectroscopy (FTIR) measurements (Fig. 3(a)) reveal that the addition of CuNWs result in the disappearance of
Fig. 2. Properties of CuNW-GO thin film. (a) Scanning electron microscopy (SEM) image of GOs coated with CuNWs having concentrations of 2 ml each. (b) Cross-section image of CuNW-GO thin film of concentration 2 ml each. (c) AFM image of the 4 ml CuNW-2 ml GO thin film. (d) Coverage density of CuNWs per cm² in the thin films. (e) CuNWs of concentration, 2 ml with an average roughness of 100 nm. (f) GOs of concentration, 2 ml with an average roughness of 36 nm.
O-H bond in GOs and confirm the binding of CuNWs to the GOs through these bonds (stretching band at 3340 cm$^{-1}$).

UV-visible absorption spectra of the GO and CuNW-GO thin films have been taken in the wavelength range of 250 to 800 nm and is given in Fig. 3(b). GOs is characterized by the presence of a broadband absorption around 250 nm which is attributed towards the $\pi \rightarrow \pi^*$ transitions of the sp$^2$ carbon atoms in the aromatic planar network of GOs [13]. CuNWs on the other hand exhibit a broadband absorption in the visible region around 540 nm due to the interband transitions or excitation of SPRs [35].

We can confirm the presence of CuNWs and GOs from the simultaneous absorption peaks in the spectra. It is observed that as the addition of the GOs on the CuNWs result in the redshift of the absorption band of GOs and blueshift of the absorption band of the CuNWs due to the increase of the scattering centers from the CuNWs. Further optical bandgap shift is calculated from the absorption spectra using the Tauc plot [36] as given in Fig. 3(c). The observed shift from 3.15 to 1.5 eV which enhances the use of this heterogeneous film as an integration material for the photonics and tunable optoelectronics.
Time-resolved PL studies are performed to get a detailed understanding of the interaction of CuNWs with GOs as given in Fig. 3(d) using an excitation wavelength of 325 nm. Strong photoluminescence or fluorescence is observed around 460 nm which is one of the prominent PL peaks of the GOs reported in the literature [37]. Eda et al. points towards the $\pi \rightarrow \pi^*$ transitions of the sp$^2$ carbon atoms in the GO atomic structure as the responsible factor for this blue PL band [38]. The observed broadening and redshift of the PL peak can be explained using the excitation wavelength dependent giant red-edge effect for the blue bands as proposed by the Cushing et al. [39].

The presence of multilayer GOs in the CuNW-GO thin films is confirmed using the Raman measurements (Fig. 3(e)) with an $I_G/I_D$ ratio of 1.1. Besides, it can be seen that as the concentration of CuNWs increase, the prominent peak intensity of G and D bands at 1580 and 1360 cm$^{-1}$ of GOs increases along with a broadband 2D peak intensity at 2700 cm$^{-1}$. Refractive index, $n$ measurements using ellipsometry shows a decrease from 1.6 to 1 when the concentration of the CuNW increases (Fig. 3(f)). It can lead to enhanced saturable absorption in these thin films and find application in nonlinear photonics. It is noted that as the concentration of the CuNWs is increased above the optimum threshold amount leading to the inhibition of the intrinsic properties of the GOs, for example, 4 mL of CuNWs to a 2 mL of GOs.

A fundamental understanding of the interaction behavior of the CuNWs and GOs can be summarised as follows. Excitation of the SPR of the metallic CuNWs can result in the energy transition to the conduction band of the GOs leading to the saturable absorption (SA) and thus the non-linear properties of the film, which will be discussed in the next session. The first-principle calculation by Subrahmanyan et al. [40] supports this theory by considering the extension of the intermediate energy states to the conduction band of the graphene in graphene-metal composites.

### 3.3. Non-linear properties

Laser-induced excitation of GOs in the nano, pico, and femtosecond regime have been demonstrated to have non-linear properties (NLO) which is contributed by the saturable absorption (SA) as well as multiphoton absorption [41]. It can be observed that the lower fluences lead to an excited saturable absorption (ESA) and higher fluences lead to a reverse saturable absorption (RSA). These properties can be widely used in nonlinear photonics [16], optical limiting devices [42], and optical switches [43]. However, for these applications, it is preferable to have large NLO properties. Recently, it is reported that the metal nanomaterials with GOs can enhance the intrinsic linear and NLO properties [44,45].

We have conducted open aperture (OA) and closed aperture (CA) Z-scan measurements in the same experimental conditions (Fig. 4) to understand the NLO properties of CuNW-GO thin films at a wavelength of 800 nm in the femtosecond regime using various concentrations of the thin films and laser fluences from 0.5 to 3 $\mu$J/cm$^2$. Enhanced SA effect is observed from the CuNW-GO thin films in comparison with the GO thin films. As the laser beam fluence increases, the RSA effect contributed by the two-photon absorption can be seen as a valley formation in the centre of the transmission maximum in Fig. 5(a).

From OA Z-scan measurements, the nonlinear absorption, $\beta$ which is a concentration-dependent parameter is calculated with the fitting of the data using the formula described in nonlinear theory as given below:

$$T = \frac{1}{\pi} \int_{-\infty}^{+\infty} \ln \left[ 1 + \frac{\beta L_{eff} I_0}{1 + \frac{z^2}{z_0^2}} \exp(-t^2) \right] dt$$

(1)
where $T$ is the normalized transmittance, $I_0$ is the peak on-axis irradiance at the focus, $z_0$ is the Rayleigh length, and $L_{\text{eff}}$ can be defined as the path length of the sample [46]. A remarkable increase of 43% of $\beta$ is observed with the addition of CuNWs to GOs as shown in Fig. 5(b).

CA Z-scan measurements in GO and CuNW-GO thin films are performed to calculate the nonlinear refraction, $n_2$ effect. A peak-valley Z-scan trace is resulting from the division of the CA Z-scan data by the OA Z-scan data for GO thin film of concentration, 2 ml and CuNW-GO thin film of concentrations 2 ml each is given in Fig. 5(c). The obtained spectral behavior is similar to other concentrations, and the obtained data is fitted using the formula, [46]

$$T(x) = 1 + \frac{4x\Delta\Phi}{(1 + x^2)(9 + x^2)}$$

where $x = z/z_0$ is the normalized position to the centre of focus and $\Delta\Phi = (2\pi/\lambda)n_2LI_0$ with L and $I_0$ are the sample thickness and peak-on-axis intensity which are estimated to be $\sim 100$ nm. Both samples exhibit a prefocal peak and postfocal valley indicating the nonlinearity of the samples to be negative.

It is reported that the population redistribution of $\pi$ electrons and the free carriers of the sp$^2$ domain mainly contributes to the nonlinear refraction, $n_2$ of GOs [47]. During the excitation of CuNW-GO thin films, carriers are possible to be transferred to the conduction band of CuNWs. The slow relaxation of the excited carriers from the metal states to the valence band of the GOs can cause carrier density enhancement in the excited states which can result in the $n_2$ (Fig. 5(d)) [41].

Further, the optical limiting (OL) property of these heterogeneous thin films is calculated from the OA Z-scan measurements using the position dependent input laser beam fluence. The OL threshold can be defined as the input laser beam fluence for which the sample transmittance is 50%. The input fluence can be calculated as follows,

$$F_{\text{in}} = \frac{4\sqrt{\pi \ln 2} E_0}{\pi^2 \omega_0^2 (1 + \frac{z}{z_0})}$$

where $F_{\text{in}}$ is the input laser fluence, $E_0$ is the used laser energy, and $\omega_0$ is the laser beam radius at the focus. The OL properties of CuNW-GO are better than that of GO thin film due to the increase of scattering centers contributed by the CuNWs (Fig. 5(e)). These results confirm the
Fig. 5. (a) Open aperture Z-scan measurement and theoretical curves of GO and CuNW-GO thin films with different concentrations using a femtosecond laser beam fluence of 2 $\mu$J/cm$^2$ at a wavelength of 800 nm. (b) Nonlinear absorption, $\beta_{\text{eff}}$ at various laser fluences using different concentrations of CuNW-GO thin films. (c) Closed aperture Z-scan measurement and theoretical curves of GOs. (d) Closed aperture Z-scan measurement and theoretical curves of CuNW-GO thin films with different concentrations using a femtosecond laser beam fluence of 2 $\mu$J/cm$^2$ at a wavelength of 800 nm. (e) Nonlinear refractive index, $n_2$ at various laser fluences using different concentrations of CuNW-GO thin films. (f) Optical limiting properties of the GO thin film with 2 ml concentration and CuNW-GO thin film with a concentration of 2 ml each.
decrease of the linear refractive index, $n$ of the thin film as shown in Fig. 3(f) with higher concentrations of CuNWs with 2 ml concentration of GOs beyond 700 nm wavelength since the nonlinear optical properties are inversely proportional to the linear refractive index [48]. The nonlinear properties of GOs we observed at a wavelength of 800 nm, is a collective influence of CuNWs instead of the peak intensity expected in the case where nanowires of only a particular dimension are present.

3.4. Transparent conductive electrodes

Here we demonstrate the use of CuNW-GO thin film as a TCE (Fig. 6(a)) which acts as an oxidation barrier for the CuNWs and can be a practical solution to overcome the expensive nature of other metallic alternatives. Figure 6(b) represents the optical transmittance and a sheet resistance of these films. The sheet resistance can be reduced to 10 Ohm/sq with an optical transmittance of 75%. The maximum optical transmittance of 93% and a sheet resistance of $10^2$ Ohm/sq is observed for the thin film having 1 ml CuNWs and 2 ml of GOs. These results can be compared to the performance achieved with the maturity attained technology using expensive metallic nanowires like silver or gold [49].

It is necessary to understand the oxidation resistance of CuNW-GO thin film, and we conducted the aging test for a longer time at room condition and under the extreme conditions of temperature around 80°C and humidity 85% for 2 hours in an oven. The monitoring of these thin films at room conditions (Fig. 6(c)) shows that in the presence of GO film the sheet resistance is
maintained to be almost $10^2$ Ohm/Sq under various concentrations of CuNWs whereas the sheet resistance of thin film with CuNWs along increased to $10^4$ Ohm/sq. From Fig. 6(d), it can be seen that the GO coating results in the oxidation of CuNWs with a sheet resistance reduced to $10^2$ Ohm/sq in comparison with CuNWs. We limited the studies to 2 hours since further prolonged exposure to extreme conditions; temperature of 80°C and a humidity of 85%, results in the melting of CuNWs and rendering the electrodes non-conductive. The prolonged endurance of the electrodes in high heat and humidity conditions and their resilience towards oxidation and melting can be attributed to the GO coating. The bare CuNW coated glass substrate degrades very rapidly and survives less than 20 minutes, as shown in Fig. 6(d).

Further, we conducted simulation studies using Lumerical commercial software to understand the plasmonic enhancements in CuNWs of thickness varying from 5 to 100 nm and width 5 to 100 nm along with a GO coating of varying thickness from 1 to 10 nm. The transverse and longitudinal modes of Copper are at wavelengths 532 nm and 750 nm [35]. In this numerical study, we considered different shapes of CuNWs having round, rectangular and triangular shape. A simulation unit consists of periodic boundary conditions (Fig. 7(a)) with a mesh size of $\lambda/40$ nm. Plane wave sources of wavelengths, 532 nm, and 790 nm are used for the surface plasmon excitations to consider the dimension dependent resonance wavelength shifts which can

![Fig. 7](image-url)

**Fig. 7.** (a) Schematic of the simulation studies on the CuNW-GO thin films. (b) Plasmonic enhancement observed with a periodicity of 100 nm for CuNW-GO arrangement with a thickness of CuNW $\sim$100 nm and GO thickness $\sim$5 nm using a plane wave source of 532 nm. (c) Plasmonic enhancement observed with a periodicity of 100 nm for CuNW-GO arrangement with a thickness of CuNW $\sim$ 100 nm and GO thickness $\sim$ 5 nm using a plane wave source of 750 nm.
be calculated from the Gan’s theory [50,51]. For a CuNW of length 150 µm which is similar to the maximum length of nanowire used in the experimental conditions, the observed transverse and longitudinal modes are at 540 nm and 750 nm. It is observed that the CuNWs with a rectangular shape as shown in Figs. 7(b) and 7(c), with a thickness of 100 nm, the periodicity of 100 nm and GO thin film coating of thickness 5 nm, a plasmonic enhancement of 15% and 20% are observed for both excitation wavelengths. This observation implements the chances of utilizing these thin films in applications like optoelectronics and plasmonics.

4. Conclusions

In summary, we have shown promising CuNW-GO thin films which are stable, temperature resistant and oxidation resistant with an optical transmittance up to 93% and sheet resistance, 10 Ohm/sq and an optical bandgap opening of 3.5 eV can be utilized as a cheaper alternative for TCEs in optoelectronic applications. Besides, enhancement of GOs NLO properties to a considerable amount of 43% with the addition of CuNWs contributed from the surface plasmon coupling demonstrates its potential usage in lightweight nonlinear photonic fibers and on-chip optical communications.

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