Organic-inorganic nanohybrids for low-powered resistive memory applications

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Abstract. Organic-inorganic nanohybrids consisting of mutually complementing conducting and semiconducting materials have received much consideration in the field of resistive switching (RS) memory devices. Herein, we report a simple and cost-effective hydrothermal method for the synthesis of reduced graphene oxide (rGO)-semiconductor (SC) nanohybrid materials by varying the semiconducting component. In this work, the sulfur based semiconductors such as ZnS, CuS and SnS are chosen owing to their unexploited nature in the field of resistive memory devices. The synthesized materials are analysed through optical and structural techniques in order to confirm their successful formation. The synthesized nanohybrids are then dispersed into polymer matrices (PMMA) and the RS memory properties are studied through current-voltage measurement. The best result of low set/reset voltage (V_{set}/V_{reset}) ~ -1.10/+1.29 V, low set/reset power consumption (P_{set}/P_{reset}) ~ 4.80 × 10^{-5}/1.16 × 10^{-4} Wcm^{-2} and high current ON/OFF ratio (I_{ON}/I_{OFF}) ~ 10^5 is exhibited by the rGO-CuS nanohybrid. Finally, a conduction mechanism based on the phenomenon of charge carrier trapping and de-trapping is proposed to explain the RS properties.

1. Introduction
Organic-inorganic heterostructures have received considerable attention owing to their wide range of applications in the field of photocatalysis, supercapacitors, solar cells, and so forth. Due to synergistic interfacial effect, the heterostructure nanohybrids display superior performances as compared to their individual counterparts which further widens their applicability in many electronic devices. Recently, the heterostructures of organic materials especially graphene oxide (GO) and its derivatives plus various inorganic semiconducting materials have received tremendous attention by researchers. The advantageous features of GO or rGO such as large specific area, high mechanical flexibility, environmental stability, high solubility etc. [1] can be exploited thoroughly by combining with suitable semiconducting materials. The favourable band edge positions and energy band gap of the semiconductor can regulate the carrier transport direction in the nanohybrids. In addition, the GO based hybrids have found applicability in the field of memory devices as well due to their cost-effectiveness, easy processability, high stability, and so forth. In the recent years, there have been numerous reports on the use of hybrid materials primarily in the field of resistive switching random access memories (RRAM). Anoop et al. recently used graphene oxide-zinc oxide (GO-ZnO) nanorods hybrid as an active layer in RRAM devices that exhibited a high I_{ON}/I_{OFF} ratio of ~ 3.3×10³ [2]. Other reports on GO-ZnO hybrid materials were made by Kapitanova et al. and Khurana et al. where both the groups were able to obtain resistive RS properties with current ratio (I_{ON}/I_{OFF}) in the range ~ 10²-10³ [3,4]. Apart from ZnO, GO based hybrids with other conducting and semiconducting materials such as molybdenum disulfide (MoS₂) [5], titanium dioxide (TiO₂) [6], gold nanoparticles (Au NPs) [7,8] etc. were found to display...
exceptional memory properties as well. For instance, GO-MoS₂ hybrid materials have been found to exhibit low operating voltages of ~ 2V and high \( I_{\text{ON}}/I_{\text{OFF}} \) ratio of ~ 10⁴ [9], whereas an \( I_{\text{ON}}/I_{\text{OFF}} \) ratio of ~ 10² was observed for GO combination with Au NPs [8]. Despite many reports, the hybrid materials are yet to be explored by embedding into polymer matrices to show their potential candidature as active memory materials.

Thus, the present work focusses on the preparation of different GO based hybrid materials by hydrothermally functionalizing it with semiconducting sulfides such as zinc sulfide (ZnS), copper sulfide (CuS) and tin sulfide (SnS). All the nanohybrid materials are dispersed into PMMA matrix and a thin layer of polymer composite film is used as an active layer for RS memory applications.

2. Experimental procedure

2.1 Materials used
Graphite flakes, sodium nitrate (NaNO₃), sulfuric acid (H₂SO₄), potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂), zinc acetate (ZnC₄H₆O₄), sulfur powder, ethylenediamine, copper nitrate (Cu(NO₃)₂), sodium thiosulfate (Na₂S₂O₃), tin chloride dehydrate (SnCl₂.2H₂O), thiourea CS(NH₂)₂, hydrazine hydrate (N₂H₄.H₂O). All the chemicals were used as received without any further purification.

2.2 Material synthesis
GO was synthesized by following the conventional Hummer’s method [10]. For the synthesis of the rGO-semiconductor (SC) hybrid materials, equal amounts of the synthesized GO sheets were initially dissolved into different solvents to be used for the individual synthesis procedure of each hybrid material through ultrasonication. The solvents for the synthesis of each hybrid material include the use of ethylenediamine, de-ionized (DI) water and N₂H₄.H₂O for rGO-ZnS, rGO-CuS and rGO-SnS preparation, respectively. The next step involved the addition of both cationic and anionic precursors to the respective GO solutions. For the same, ZnC₄H₆O₄ and sulphur powder were added to the GO solution in ethylenediamine to yield the rGO-ZnS hybrid whereas for the preparation of the rGO-CuS hybrid, Cu(NO₃)₂ and Na₂S₂O₃ were added to the GO/DI water solution. In a similar manner, SnCl₂.2H₂O and CS(NH₂)₂ were respectively used as the source of tin and sulphur for the synthesis of rGO-SnS hybrid material and were added to the solution of GO in N₂H₄.H₂O. All the solutions were then subjected to vigorous stirring for 4 h and were then transferred to individual teflon lined stainless steel autoclaves. The autoclaves were then heated at a temperature of 180 °C for 12 h in a hot air oven. The high temperature synthesis assisted the formation of semiconducting components in the GO vicinity and simultaneously converted the GO into rGO which is expected to further enhance the materials’ electrical properties. After cooling down the solutions to room temperature, the solutions were repeatedly washed with DI water and ethanol to remove the impurities and the precipitates were then collected and dried at ~ 50 °C to obtain the final powders of the rGO-SC hybrids. The as-synthesized hybrid powders were characterized with the help of field emission scanning electron microscopy (FE-SEM; JEOL JSM-7600F) and transmission electron microscopy (TEM; JEOL JEM 2100F).

2.3 Device fabrication
The active layer of the devices comprises of an rGO-SC hybrid/polymethyl metacrylate (PMMA) composite where the rGO-SC nanohybrid is the charge transporting material and PMMA would behave as the charge blocking one. For the same, three separate solutions each containing 99.9 mg of PMMA in 3 ml of toluene were prepared through ultrasonication. In the next step, 0.1 mg of each synthesized rGO-SC hybrid material were added to the PMMA solutions and were subjected to further ultrasonication. The final solutions of rGO-SC hybrid/PMMA were then spin-coated onto pre-cleaned indium tin oxide (ITO) coated glass substrates at 9000 rotations per minute (RPM) for 60 s by using a programmable spin coating unit (Apex Instruments, Model: Spin NXG P2). The spin-coated ITO substrates were then vacuum dried at R.T. in a horizontal tube furnace fitted with a vacuum pump. Finally, aluminium (Al) was deposited as a top electrode by using a shadow mask technique in a thermal evaporation unit (HindHivac, Model: 12A4DM). The fabricated devices were named as RZNPC, RCUPC and RSNPC corresponding to the use of rGO-ZnS, rGO-CuS and rGO-SnS hybrid materials in the devices’ active layer, respectively and the R.T. J-V analysis was performed by using a Keithley
4200 semiconductor characterization system. A schematic diagram of the fabricated ITO/rGO-SC/PMMA/Al device is shown in figure 1.

![Schematic diagram](image)

**Figure 1.** Schematic diagram of ITO/rGO-SC hybrid/PMMA/Al devices.

3. **Results and discussion**

3.1 **Photoluminescence (PL) spectroscopy**

The PL spectra of all the synthesized rGO-SC hybrid materials is shown in figure 2. From the figure, it can be seen that all the hybrids share a common peak at ~ 334 nm which corresponds to the transition of electrons from the δ to π* energy orbitals of rGO [11]. Thus, the peaks are indicative of the conversion of GO to rGO during the high temperature hydrothermal synthesis process. Furthermore, additional low intensity peaks with different positions appear for each nanohybrid material such as at ~ 520 nm for rGO-ZnS, ~ 433 nm for rGO-CuS and ~ 412 nm for rGO-SnS. All these peaks correspond to some sort of defects present in the semiconducting component of the hybrid materials. For instance, the low intensity peak in the spectra of rGO-ZnS hybrid appears due to the presence of zinc vacancies in it [12]. In a similar manner, the less intense peaks in rGO-CuS and rGO-SnS result from the presence of native defects and tin vacancies, respectively [13,14].

![PL spectra](image)

**Figure 2.** PL spectra of (a) rGO-ZnS (λ_ex = 270 nm), (b) rGO-CuS (λ_ex = 300 nm) and (c) rGO-SnS hybrid materials (λ_ex = 300 nm)

3.2 **Field emission scanning electron microscopy (FE-SEM)**

The field emission scanning electron microscopy (FE-SEM) images of the rGO-SC hybrid/PMMA composites thin film is shown in figure 3(a-c). From the figures, it can be seen that all the three hybrid materials display identical topographical features with a distribution of irregularly shaped particles. It has been reported that GO or rGO possess a sheet like structure whereas films of pure PMMA contain a lot of voids [10,15]. However, such deviated results in the present study may be due to the wrapping of the rGO-SC hybrids by PMMA upon ultrasonication.
Figure 3. (a-c) FE-SEM images and (d-f) TEM images of rGO-ZnS, rGO-CuS and rGO-SnS hybrid materials, respectively.

3.3 Transmission electron microscopy (TEM)
Figure 3(d-f) represent the transmission electron microscopy (TEM) images of the synthesized rGO-SC hybrids. From the TEM image of rGO-ZnS (Fig. 3(d)), it can be seen that ZnS has a spherical structure with rGO sheets wrapped around it. In contrast, the TEM images of rGO-CuS and rGO-SnS nanohybrids [Fig. 3(e) and 3(f)] show that the different sized CuS dots are distributed all over the rGO sheet whereas the SnS forms rod shaped structure wrapped with rGO sheets. However, the agglomeration of the semiconducting component on the rGO sheets restrict the transmission of electrons through it, due to which no proper image of the SC crystal planes could be obtained.

3.4 Current density-voltage (J-V) analysis
The J-V characteristics of all the fabricated devices (ITO/rGO-SC/PMMA/Al) for a single sweep is shown in figure 4. At low negative voltage values, all the devices exhibit a slow initial rise in current which corresponds to the OFF or high resistance state (HRS) of the devices. However, all the devices undergo a sharp increase in current at a threshold voltage which marks the transition of the devices from the OFF to the ON or low resistance state (LRS). The transition from the OFF to the ON state corresponds to the write mechanism of the device and the corresponding threshold voltage at which the transition occurs is called the set voltage (V_{set}). Further increase in the negative voltage does not change the current value and the devices continue to retain their ON state even when the bias voltage is reduced to zero which further establishes their non-volatile nature. However, upon applying a positive voltage, all the devices initially maintain the ON state until a particular voltage called the reset voltage (V_{reset}) is reached after which the current in the devices undergo a sharp fall. This phenomenon represents the transition of the devices back to the OFF state and is equivalent to the erase mechanism of a memory device. Such transitions of the devices from the OFF to the ON state at negative applied voltage and returning back to the OFF state upon altering the voltage polarity are representative of their bipolar RS nature.
Figure 4. J-V characteristics of the fabricated ITO/r GO-SC/PMMA/Al devices for the 1st sweep. Arrows indicate the direction of sweep i.e., 0 → –V → 0 → +V → 0.

Considering the conduction of charge carriers through the assembly of PMMA, rGO and the semiconducting material, it is to adhere that all the three semiconducting materials used in this study viz. ZnS, CuS and SnS as well as rGO contain defects and vacancies which act as trap sites for the charge carriers. Thus, upon negatively biasing the top Al electrode, electrons start to move from Al to ITO. However, at the initial phase of low bias, the electrons get trapped in the defect sites present in the rGO sheets and semiconducting component of the hybrid material. At this time, the devices remain in the OFF state and the process of electron trapping continues until all the trap sites get completely filled. Once a trap free environment is achieved, a large number electrons from Al can move smoothly through the active layer and reach the ITO electrode which switches the device to the ON state. Upon altering the voltage polarity, the direction of electron flow gets altered in addition to the de-trapping of the electrons from the defect sites which destroys the trap free environment and terminates the smooth flow of electrons through the devices. The cease in the electron flow results in the transition of the device from the ON to the OFF state. Furthermore, from the figure 5(a), it can be seen that the V_{set} and V_{reset} is lowest for the RCUPC devices followed by the RSNPC and finally the RZNPC devices. Such a trend may be due to the gradually increasing conductivity from ZnS → SnS → CuS as already reported [16-18]. Now, considering the use of equal amounts of GO and identical synthesis conditions during the preparation of each hybrid material, it is expected that the nature of the semiconducting component plays a major role in the overall electrical properties of the rGO-SC hybrid materials. Thus, the highest conductivity of CuS amongst all three semiconductors allows the easy flow of charge carriers through the rGO-CuS hybrid as compared to the two other hybrid materials. The higher charge carrier mobility enables the early filling up of trap sites in the RCUPC device which switches ON the device at extremely low voltages. In a similar manner, the relatively higher conductivity in the RSNPC than the RZNPC device results in the OFF → ON transitions at a lower voltage for the former. Furthermore, the greater resistivity of ZnS demands the supply of higher positive voltage in order to release the trapped electrons and move them to the top Al electrode which in turn increases its reset voltage. The phenomenon applies to the other hybrid materials as well and as such, the V_{reset} decreases with the decrease in resistivity of the semiconducting material thereby following the trend V_{reset} (RCUPC) < V_{reset} (RSNPC) < V_{reset} (RZNPC). Figure 5(b) shows the consumption of power by each device during the set (P_{set}) and reset (P_{reset}) processes. From the figure, it can be seen that the RCUPC device exhibit the lowest power consumption for both the processes which is in accordance with the low V_{set} and V_{reset} displayed by it. Table 1 summarizes the memory parameters obtained for all the three fabricated devices.
Figure 5. (a) Variation of $V_{\text{set}}/V_{\text{reset}}$ and (b) $P_{\text{set}}/P_{\text{reset}}$ with the change in rGO-SC hybrid in the device’s active layer.

Table 1. Memory parameters obtained for the fabricated ITO/rGO-SC hybrid/PMMA/Al devices.

| Device  | $V_{\text{set}}/V_{\text{reset}}$ (V) | $P_{\text{set}}/P_{\text{reset}}$ (Wcm$^{-2}$) | $I_{\text{ON}}/I_{\text{OFF}}$ ratio |
|---------|-------------------------------------|---------------------------------------------|-----------------------------------|
| RZNPC   | $+4.92$                             | $1.14 \times 10^{-2}/2.15 \times 10^{-4}$   | $10^3$                            |
| RCUPC   | $+1.29$                             | $4.80 \times 10^{-5}/1.16 \times 10^{-4}$   | $10^3$                            |
| RSNPC   | $+1.50$                             | $1.57 \times 10^{-4}/2.80 \times 10^{-4}$   | $10^3$                            |

4. Conclusion

The rGO-SC nanohybrid materials were successfully synthesized by using different semiconducting materials in a simple and cost-effective hydrothermal process. The FE-SEM images of the synthesized materials exhibited the presence of irregular particles due to the PMMA wrapping over the hybrid materials. The TEM images showed that despite of identical synthesis conditions, all the three semiconducting components of the hybrid materials were differently shaped such as spherical for ZnS, dot like for CuS and rod shaped for SnS. The TEM images however showed that all the semiconducting materials were grafted on the rGO sheets which further confirmed their successful growth in GO vicinity. The J-V analysis showed that all the rGO-SC hybrids possess RS properties and RCUPC device being the best performing amongst all with $V_{\text{set}}/V_{\text{reset}}$ of $-1.10/1.28$ V and $I_{\text{ON}}/I_{\text{OFF}}$ ratio of $10^3$. The charge carrier trapping and de-trapping can be considered responsible for the RS properties in all the fabricated hybrid devices. However, further modifications in the synthesis of rGO-ZnS and rGO-SnS hybrids or fabrication of RZNPC and RSNPC devices may improve their memory properties. The exceptional performance of the RCUPC device with further scope of improvement suggests the potential candidature of the hybrid in the next generation memory devices.

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