Chapter 7

Reduced Graphene Oxide Based Semiconductor Nanostructures*

Summary

Hybrids of rGO with semiconductor nanostructures such as metal oxides and metal sulfides were synthesized using simple chemical methods involving solution phase, hydrothermal and liquid/liquid interface and their structural and optical properties were studied. The as-prepared composites are explored as photocatalysts and reusable SERS substrates. This chapter consists of three sections.

In the 1st section, the influence of composition, morphology and defects on the photocatalytic activity of binary and ternary hybrid systems of rGO-ZnO and rGO-Au-ZnO are presented. ZnO possessing various morphologies such as nanoparticles and nanorods on rGO and rGO-Au are obtained by solution phase and hydrothermal methods involving hydrolysis of zinc acetylacetonate in the presence of GO. Photocatalytic degradation studies of rhodamine B dye reveals that all the ZnO hybrids show higher degradation rates that bare ZnO. The photodegradation rates follow the order rGO-Au-ZnO NPs > rGO-ZnO NPs > rGO-Au-ZnO NRs > rGO-ZnO NRs > bare ZnO NPs. The kinetics of photocatalysis under various incident UV power intensities has also been studied. The difference in kinetics of ZnO hybrids is correlated with the observed photoluminescence, which is reflected as quenched band edge and defect emission arising from the charge transfer between rGO, ZnO, and Au leading to suppression in exciton recombination rates. Various factors such as structure, morphology, charge transfer and adsorption are considered to explain the observed kinetics. The photocatalytic rate variation with incident UV power is also expressed. The enhanced photodegradation achieved by metal oxide nanostructures when combined with rGO or metal nanoparticles can be exploited to regenerate used SERS substrates for dyes. In the 2nd section, reusable SERS substrates based on multifunctional rGO-metal oxide nanostructures and metal nanoparticle doped systems are presented. The hybrids are prepared in the form of free-
standing thin films at a liquid/liquid interface continuous over a large area utilizing interfacial hydrolysis and self-assembly. The as-synthesized hybrid films such as rGO-ZnO, rGO-Ag-ZnO, rGO-CuO and rGO-SnO$_2$ exhibit unique morphologies like hexagonal cylinders, rice shaped, elongated splinters and spheres respectively, interspersed with rGO layers. The synergic effect due to charge transfer between metal oxide, rGO and dye causes chemical enhancement of dyes and fluorescence quenching. Doping with Ag nanoparticles improves SERS enhancement factor and detection sensitivity exploiting the electromagnetic enhancement from Ag surface plasmons. These hybrid films could clean themselves via photocatalytic degradation of adsorbed organic dyes under UV light in wet condition. The observed SERS enhancement for rhodamine 6G dye on rGO-Ag-ZnO is $\sim 1 \times 10^4$, and the SERS enhancement factors are in the order rGO-Ag-ZnO > rGO-CuO > rGO-ZnO > rGO-SnO$_2$ NP hybrid films.

Liquid/liquid interface method can also be employed to obtain rGO based metal sulfide nanoparticle films and is illustrated with respect to rGO-silver sulfide in the 3rd section. Free standing, ultra-thin films of Ag$_2$S and rGO-Ag$_2$S hybrids are synthesized employing in situ chemical reaction strategy. rGO-Ag$_2$S exhibit interesting optical and electrical properties. The hybrid films absorb in the visible region 500-650 nm and show the emission in the red region. A higher conductance is observed for the as synthesised hybrid films arising from the rGO component.

7.1 Introduction

Semiconductor materials possess fundamental energy band gap between that of metal and insulators. In semiconductors, the valence band is completely filled with electrons and the conduction band is empty. These semiconductors consisting of metal oxides and metal sulphides are technologically important materials for many applications including nanoelectronics, nanophotonics, energy conversion, solar cells, photocatalysis, detectors, SERS and chemical sensors. The most attractive properties of these semiconductors can be tuned by changing the morphology and size. When the size of the semiconductor particles is reduced to the nanoscale, their physical and chemical properties vary significantly, resulting in unique properties due to their large surface area and quantum confinement effect. Many semiconductors such as ZnO, SnO$_2$, CuO, TiO$_2$, ZrO$_2$, SrTiO$_3$, MoS$_2$, Fe$_2$O$_3$, Ag$_2$S, ZnS, CdS, and WO$_3$, etc., have been studied as dynamic photocatalysts for the degradation of organic contaminants present in the water. The properties of these materials can be improved by combining with carbon nanomaterials and metal nanoparticles.

Graphene and rGO are broadly used as a platform to assemble a variety of metal and metal oxide nanostructures to generate functional materials with unique properties. rGO is known to its high surface area, atomic thickness 2D nature and flexibility. High surface area and remnant oxygen functional groups present on the basal plane of rGO promote adsorption of various molecules and anchoring of nanostructures while carbon network of rGO helps delocalisation and shuttling that aids in fluorescence quenching and photocatalysis. Metal or semiconductors nanostructures with desired properties such as photoexcitation, photoconductivity, charge transfer, surface plasmon resonance or magnetism may be chosen to be adsorbed on the surface of rGO layers. Hence, a synergic effect between the adsorbed metal or semiconductor nanostructures and the rGO layer can
impart the unique properties to these materials. Assembly of multiple nanostructures with various functions on rGO is a significant step towards the fabrication of multifunctional nanomaterials.\(^{(18)}\)

Generally, rGO based multifunctional materials are prepared by chemical methods such as microwave refluxing, sol-gel, hydrothermal, spray pyrolysis and precipitation, etc.,\(^{(19-24)}\) as they provide a simple and cheap route to obtain large quantities of these materials. We have also employed chemical methods such as solution phase, hydrothermal and liquid/liquid interface to synthesize rGO-metal oxide and metal sulphide nanomaterials. We have chosen rGO based ZnO, CuO and SnO\(_2\) and rGO-Au/Ag-ZnO to demonstrate the properties and applications of these materials.

ZnO is a wide bandgap semiconductor (3.37 eV) with a high absorption and luminescence in the ultraviolet (UV) region, has a stable wurtzite crystal structure. It has large exciton binding energy (60 meV) and has potential applications in the field of photovoltaics and photocatalysis.\(^{(1)}\) Copper oxides are available in two stable forms such as cuprous oxide (Cu\(_2\)O) and cupric oxide (CuO). These two oxides have two different colours, crystal structures, physical and electrical properties. CuO is a p-type semiconductor having a narrow direct band gap of 1.2 eV (bulk) and a monoclinic structure. It is an attractive material because of its availability, non-toxicity, and it can be prepared by low-cost solution based methods, which are the major reasons to use them for sensing applications.\(^{(25)}\) SnO\(_2\) is a transparent, wide band gap n-type semiconductor with a reported band gap of 3.6 eV (bulk) at room temperature. SnO\(_2\) has a tetragonal rutile structure. Its unit cells contain two Sn and four oxygen atoms; Sn atom is at the centre of six oxygen atoms placed at the corners of a regular octahedron. Every oxygen atom is surrounded by three Sn atoms at the corners of an equilateral triangle. If SnO\(_2\) is entirely stoichiometric, it would be an insulator. However, the reasonable number of
Silver sulphide (Ag\textsubscript{2}S) is a dark gray coloured and mixed conductor material with a band gap of 1.0 eV (bulk). The conductivity of the system is due to the transport of both Ag\textsuperscript{+} and electrons. Ag\textsubscript{2}S corresponds to the family of silver chalcogenides such as Ag\textsubscript{2}Se and Ag\textsubscript{2}Te. The structure of these materials is usually a rigid body centred cubic (bcc) lattice. The Ag\textsuperscript{+} ions are distributed in octahedral and tetrahedral positions in the lattice. The number of octahedral and tetrahedral sites availability is always much higher than the Ag\textsuperscript{+} ions so the Ag\textsuperscript{+} ions always move to the vacant sites. This results in high ion mobility in these materials.

The photodegradation efficiency of metal oxide depends on the generation of electrons (conductance band) and hole (valence band) under UV light irradiation, which combine with oxygen and hydroxyl ions to form free radicals that react with the dye molecules. Photocatalytic activities of ZnO has been reported to be significantly enhanced when doping with noble metals (Au, Ag) or with π conjugated systems such as carbon nanotubes and graphene. Doping shifts the optical absorption edge, improves the charge transfer across the components and reduces the recombination rates. It can also promote visible light absorption of metal oxide systems enabling visible light photocatalysis. Introducing the defect levels or charge transfer states in the metal oxide systems can suppress the recombination effects. The defect engineering in the parent ZnO material in the form of oxygen, zinc vacancies or interstitials as trap states is shown to promote charge separation. Combining ZnO and carbon nanostructures provide alternate charge transfer pathways prolonging the lifetime of electrons and holes. Thus, Au-ZnO and Ag-ZnO hybrid nanostructures are found to be efficient photocatalysts that the bare ZnO. There are several reports on the efficiency of ZnO hybrids with carbon materials for the photocatalytic degradation of organic molecules and is facilitated by the excited state electron transfer from ZnO to carbon materials. Earlier reports...
showed that various preparation methods significantly influence the morphology of ZnO nanostructures and also defect states. (29-34) There are only a handful of reports available on combining ZnO with rGO and metal nanoparticles for improved photodegradation.

Metal oxide nanostructures are also considered interesting to explore SERS for the detection of molecules. These materials cause Raman enhancement due to charge transfer between the molecules and metal oxide and is often studied to explore the adsorbate interaction with the nanostructure. In this case, the attractive feature of photodegradation and SERS can be combined to obtain recyclable substrates. However, chemical enhancement provided by metal oxides are of the order $10^2$ when compared to electromagnetic enhancements ($10^6$) provided by metal nanoparticles. Therefore, doping metal oxide systems with metal nanoparticles can greatly improve SERS effect of hybrid systems. rGO platform can reduce the fluorescence background in SERS as well as contribute additionally to chemical enhancement due to hanging oxygen functionalities. (41, 42) There are only a handful of reports on reusable SERS substrates in the literature. Reusability of plasmonic substrates on thermal treatment at higher temperatures and UV-ozonolysis have been reported. (43, 44) C-doped TiO$_2$ and Ag for photoelectrochemical applications and hybrids of ZnO with rGO and Ag or Au nanoparticles are demonstrated to be recyclable by UV or visible light irradiation. (45, 46)

In this chapter, we describe the synthesis of rGO-ZnO and other rGO-metal oxide nanostructures by different chemical methods and investigate their photocatalytic properties and applications in SERS. We also present a study of Ag$_2$S and rGO-Ag$_2$S nanoparticle films.
I. Synthesis of rGO-ZnO and rGO-Au-ZnO nanostructures and their photocatalytic activity in relation to composition and morphology

7.2 Experimental details

7.2.1 Materials

Bis(2,4-pentanedionato) zinc (II) monohydrate (zinc acetylacetonate; Zn(acac)$_2$.H$_2$O), ammonia (25%) solution, absolute ethanol (99.99%), hydrazine hydrate (NH$_2$NH$_2$.H$_2$O), Rhodamine B (RhB), were purchased from Sigma-Aldrich and used as received without any further purification. Exfoliated GO synthesised from graphite (-300 mesh, Alfa-Aesar) powder employing modified Hummer’s method.

rGO and rGO-Au-based ZnO hybrids are prepared by conventional solution phase and hydrothermal methods (Fig 7.1).

7.2.2 Synthesis of rGO-ZnO and rGO-Au-ZnO hybrid NPs

Initially, dispersions of rGO and rGO-Au nanoparticles were prepared by reduction of GO along with or without HAuCl$_4$. 3 mg of GO was dispersed in 25 mL of Milli-Q water and was reduced by adding 20 μL of hydrazine hydrate and heating to 100°C for 2 hrs. The yellowish brown colour of GO transformed into black colour dispersion (rGO), which is filtered, dried under vacuum and redispersed in ethanol. In the case of rGO-Au, 1 mL of 25 mM HAuCl$_4$ solution was also added to GO dispersion followed by the addition of hydrazine hydrate. rGO and rGO-Au nanoparticles prepared above was used for in-situ loading of ZnO nanostructures.

7.2.3 Solution phase deposition

rGO-ZnO NP hybrids were synthesised by adding 300 μmoles of Zn(acac)$_2$ and 600 μmoles of NH$_3$ to 25 mL ethanol containing rGO in a round bottom flask. The whole system was heated in an oil bath maintained at 120°C for 8 hrs. The product was collected, filtered, washed several times with milli-Q water and ethanol. The final product
was dried at 50 °C. For the synthesis of rGO-Au-ZnO NPs hybrids, rGO-Au NPs in 25 mL of ethanol was used instead of rGO. Bare ZnO NPs was also synthesized by the same procedure without adding rGO dispersion for performing control experiments.

7.2.4 Hydrothermal route

rGO-ZnO NRs and rGO-Au-ZnO NR hybrids were prepared under hydrothermal conditions. In a typical synthesis, 300 μmoles of Zn(acac)₂ and 600 μmoles of NH₃ were added to 20 mL of rGO dispersion in ethanol. The whole mixture was taken in a teflon-lined stainless steel autoclave (pressure vessel) and kept in a hot air oven for heating at 120°C for 8 h. After the completion of the reaction, the autoclave was cooled down to room temperature. The product was collected and washed with milli-Q water. The final product was dried at 50°C. In rGO-ZnO NRs-Au NP hybrid synthesis, rGO-ZnO NRs was synthesised by the same procedure and Au NPs were formed on rGO-ZnO NRs by hydrazine hydrate reduction of 1 mL of 25 mM HAuCl₄ solution in rGO-ZnO NRs dispersion.

Figure 7.1. Schematic representation of reaction procedure to synthesize rGO-ZnO and rGO-Au-ZnO composites.
7.2.5 Characterization

The UV-visible absorption spectra of as-prepared hybrids were obtained on Perkin-Elmer Lambda 20 spectrophotometer, for which the samples were dispersed in ethanol by sonication. The photoluminescence (PL) of prepared samples were recorded using Horiba JobinYvon, Fluorolog-3. For this, the samples were dispersed in ethanol. The surface morphology and composition of prepared composites were characterised by Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) spectra respectively. The SEM images and EDS were recorded on a Nova NanoSEM600 (FEI, The Netherlands). For SEM imaging, the samples were collected on doped Si substrate and were washed, dried under argon gas. X-ray diffraction (XRD) patterns of the samples were performed with Rigaku Smart Lab Diffractometer equipped with parallel beam optics, and Cu-Kα radiation (λ= 1.54 Å, 40 kV, 30 mA) was incident at the grazing angle 0.3°.

7.2.6 Measurements of photocatalytic activity

Photocatalytic activities of synthesised composites were evaluated by monitoring RhB degradation under UV light (HAMAMATSU L833-01 UV spot light source) of 365 nm wavelength. In a typical method, 10 mg of catalyst (ZnO or its hybrid) was added to 50 mL of 40 μM (19 ppm) RhB solution taken in a 60 mL glass beaker. Before irradiation, the solution was stirred overnight in the dark to achieve adsorption-desorption equilibrium. Absorption spectra of RhB solution before and after equilibration was also monitored. After overnight stirring, the solution was exposed to UV light. The distance between lamp and sample was maintained at 4.5 cm, corresponding to 110 mW cm⁻² for 100 % intensity of UV light. A sample of about 1 mL solution was withdrawn at regular intervals during the experiment, diluted to 3 mL and centrifuged at 3000 rpm to remove the catalyst completely. The absorbance of the centrifuged solutions at regular intervals
was monitored by recording UV-visible absorption spectra in the range 400-700 nm using Perkin-Elmer Lambda 20 spectrophotometer. For the kinetic study, the intensity of RhB absorption maxima at 556 nm with time was measured. The absolute concentrations were calculated from absorbance versus concentration plot of standard RhB solutions applying Beer-Lambert law. The photocatalytic activity of ZnO, rGO-ZnO (higher and lower loading of ZnO), rGO-Au-ZnO NPs (solution phase preparation) and rGO-ZnO NRs and rGO-ZnO NRs-Au NPs hybrid (prepared by hydrothermal) were thus measured at 100% light intensity. rGO-ZnONRs hybrid was used as a catalyst for degradation of RhB under various light intensities, 100%, 73%, 51% and 27% corresponding to 112.5, 75.1, 50.6 and 25.1 mW cm\(^{-2}\) to study the effect of UV light power on photocatalysis. The light intensity of the UV lamp was measured using a photodiode positioned at a similar distance from the source to sample.

7.3 Results and discussion

ZnO nanostructures are loaded on to rGO and rGO-Au hybrids by in situ alkaline hydrolysis of zinc acetylacetonate in ethanol employing two different methods including solution phase and hydrothermal. ZnO and Au NPs are prepared without any conscious addition of surfactant (or) organic capping agents. The as-synthesised ZnO composites are studied by XRD to know the formation of ZnO and its crystallinity. Fig.7.2 gives the XRD patterns of various rGO- ZnO composites synthesized under different conditions. In all the cases ZnO shows significant reflections at 31.8°, 34.4°, 36.3°, 47.6°, 56.7°, 62.9°, 66.4°, 67.9°, 69.2°, 72.7° and 77°corresponding to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) planes of hexagonal wurtzite structure. In rGO-ZnO NPs, a pronounced diffraction peak appears at 22° from exfoliated rGO layers along with ZnO reflections. In the case of rGO-ZnO and rGO-Au-ZnO hybrids prepared by solution route, ZnO peaks are less intense and broader due to the presence of small
NPs (Fig.1b,c). rGO-Au-ZnO NPs, rGO-ZnO NRs-Au NPs show diffraction peaks at 38.2°, 44.4°, 64.7° and 77.6° corresponding to (111), (200), (220) and (311) planes of fcc Au in addition to ZnO peaks.

Figure 7.2. XRD patterns of ZnO, rGO and rGO-Au based ZnO hybrids synthesised employing different methods a) ZnO NPs b) rGO-ZnO NPs c) rGO-Au-ZnO NPs; by solution phase deposition d) rGO-ZnO NRs e) rGO-ZnO NRs-Au NPs; by hydrothermal method.

Figure 7.3. UV-visible absorption spectra of ZnO and rGO based ZnO nanohybrids synthesised employing different methods a) ZnO NPs b) rGO-ZnO NPs c) rGO-Au-ZnO NPs; solution phase preparation. The inset shows a magnified view of ZnO band edge absorption and Au nanoparticle surface plasmon absorption in (c). d) rGO-ZnO NRs e) rGO-ZnO NRs-Au NPs; hydrothermal route.

The optical properties of as-synthesized composites are given in figure 7.3. Solution phase prepared ZnO and rGO-ZnO hybrid exhibit band edge absorption at 355 nm, almost
15 nm blue-shifted than the band gap absorption of bulk ZnO at 370 nm. The blue shift arises due to the quantum confinement effect of the smaller size of ZnO. In the case of rGO-ZnO NPs (Fig. 7.3b), the band edge absorption extends slightly to the visible region when compared with the bare ZnO. The rGO absorption band is observed in all the rGO based composites at 280 nm due to the $\pi-\pi^*$ transitions of the $sp^2$ hybridized carbon network (Fig. 7.3b-e). For rGO-Au-ZnO NPs prepared by solution phase, the band edge absorption of ZnO is observed at 360 nm along with broad absorption at 600 nm arising from surface plasmon absorption of Au NPs on rGO (see inset of Fig. 7.3). The band edge absorption of ZnO in rGO-ZnO NRs and rGO-ZnO NRs-Au NPs prepared by the hydrothermal method is observed at 373 nm, which is similar to that of bulk ZnO absorption and the absorption tail extends into the visible region. The extension of band edge absorption into the visible region indicates the presence of defect levels in the ZnO nanostructures. For rGO-ZnO NRs-Au NP composite surface plasmon absorption of Au NPs appears at 600 nm.

![PL spectra of ZnO hybrids](image.png)

Figure 7.4. PL spectra of ZnO hybrids ($\lambda_{ex}$ -325 nm) a) rGO b) bare ZnO NPs (intensity/2) c) rGO-ZnO NPs d) rGO-Au-ZnO NPs; by solution phase method and e) rGO-ZnO NRs f) rGO-ZnO NRs- Au NPs by hydrothermal method.

Photoluminescence properties of ZnO hybrids provide an understanding of the defect states and donor-acceptor levels. The PL spectra of as synthesised ZnO hybrids
are shown in figure 7.4. The excitonic emission (band-edge) from ZnO nanostructures is seen at 380 nm (indicated by an arrow) along with various defect emissions in the visible region for ZnO hybrids prepared by different routes. rGO exhibit low-intensity PL in the violet-blue region (~420 nm), which arises due to the radiative recombination of electron-hole pairs (sp$^2$ clusters embedded in the sp$^3$ matrix) (48) present in the rGO matrix. Bare ZnO NPs prepared by solution phase method exhibits intense defect emissions in the visible region at 405 nm, 430 nm and 460 nm (Fig.7.4b), which are due to the presence of intrinsic ZnO defects such as Zn vacancies and Zn interstitials. (49, 50) In the case of rGO-ZnO NPs, the defect emissions are seen even in the yellow-green region (Fig.7.4c) due to the presence of oxygen vacancies on surfaces. The band edge and visible emissions are suppressed due to the presence of rGO layers. For the rGO-Au-ZnO NPs prepared under solution phase method, the band edge peak is quenched, and the visible emissions are slightly suppressed. rGO-ZnO NRs show a luminescence in the green-yellow region, representing the presence of surface defects and oxygen interstitials. The band edge emission is still observed indicating some recombination effects. For the rGO-ZnO NRs-Au NPs, the band edge emission is present substantially, and the visible emission is also seen due to the weak interface between the rGO, ZnO, and Au. The band edge emission is reduced compared with bare ZnO but is intense than rGO-ZnO NRs and rGO-ZnO NPs. The surface morphology, distribution and composition of ZnO and ZnO hybrids with rGO and Au NPs were studied by FESEM and EDS. Fig.7.5a shows bare ZnO NPs by solution phase method. ZnO NPs appeared as spheroidal particles that aggregate and forms slightly elongated features. Similar aggregated ZnO spheroidal structures (Fig.7.5b) obtained on rGO layers during the solution phase preparation of rGO-ZnO NPs. The magnified view of rGO-ZnO NPs is given in Fig.7.5c, bunches of aggregated, elongated nanostructures appear like grain stalks. When ZnO is grown in situ on to rGO-Au NPs by
Figure 7.5. FESEM and EDS of ZnO and its hybrid materials prepared under different synthesis conditions a) ZnO NPs by solution phase (b) rGO-ZnO NPs by solution phase; ZnO NPs interspersed with rGO layers (c) a magnified view of (b); aggregated elongated ZnO NPs bunched like grain stalks (d) rGO-Au-ZnO NPs by solution phase; Au NPs (inset shows Au NPs size) and ZnO NPs on rGO layers. (e) a magnified view of (d); bright spheres are Au nanoparticles and ZnO appear as aggregated NPs f) Au NPs size histogram (rGO-Au-ZnO NPs). g) rGO-ZnO NRs by hydrothermal route; well-defined hexagonal rods of ZnO mixed with rGO sheets h) rGO-ZnO NRs-Au NPs by hydrothermal route. Insets show EDS spectra.

solution phase growth, aggregated particles are observed. Au NPs appeared as bright spheres of 30-100 nm diameter in size and interspersed with rGO layers in rGO-Au-ZnO NPs. ZnO NPs are well interfaced with Au NPs and rGO layers. The size distribution of Au NPs is shown in Fig.7.5f. EDS spectra given in the inset of Fig.7.5e display the presence of Au along with Zn, O, and carbon. rGO-ZnO NRs prepared by hydrothermal method exhibit well-defined hexagonal rods with ~20 nm diameter and 60-80 nm length on rGO layers (Fig.7.5g). Fig.7.5h shows rGO-ZnO NRs-Au NPs hybrid system prepared by deposition of Au NPs on the rGO-ZnO NRs system. ZnO NRs are well shaped, and the Au NPs are aggregated and interspersed with ZnO NRs and rGO layers. Because of higher temperature and pressure present inside the vessel, hydrothermal method produces highly crystalline, well shaped ZnO nanorods and also 3 times the greater yield of rGO-ZnO NRs is obtained compared with solution phase method for similar quantities of precursors and duration of the reaction. This indicates an efficient hydrolysis of zinc precursor and completion of reaction under hydrothermal conditions. A gravimetric assay in the lab by oxidising rGO in air gave the weight percent of ZnO: rGO roughly as 72: 28 for hydrothermally prepared rGO-ZnO NRs and 48: 52 for solution phase made rGO-ZnO NPs. The weight percentage of ZnO: rGO: Au is 50: 30: 20 for rGO-Au- ZnO NPs. the elemental composition obtained from EDS for various hybrids are given in the table 7.1. The carbon to zinc atomic ratio is lower in the case of hydrothermal product than solution
Table 7.1. Elemental composition of ZnO and its hybrids from EDS analysis.

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<th>ZnO NPs (solution phase)</th>
<th>rGO-ZnO NPs (solution phase)</th>
<th>rGO-Au-ZnO NPs (solution phase)</th>
<th>rGO-ZnO NRs (hydrothermal)</th>
<th>rGO-ZnO NRs-Au NPs (hydrothermal)</th>
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<tr>
<td>Zn L</td>
<td>70 37</td>
<td>33 9</td>
<td>39 16</td>
<td>73 38.5</td>
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<td>O K</td>
<td>30 63</td>
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phase product according to the gravimetric assay indicating larger amount of ZnO compared to rGO. The Zn to O atomic ratio is lower in the solution phase prepared bare ZnO NPs indicating a higher concentration of Zn vacancies and defects in the solution phase made hybrids. In order to show the distribution and interfacing of Au NPs with ZnO NPs and rGO layers in the ternary rGO-Au-ZnO hybrids, backscattered secondary electron imaging and EDS mapping were performed and depicted in figure 7.6. Au NPs having the highest backscattering coefficient appears as the bright spheres in the backscattered image (Fig.7.6 a,b), and ZnO particles on rGO appear less bright. EDS mapping of a selected area of the above hybrid is performed for Au M, Zn L, and C K levels. An Au M map and a composite map of C, Zn and Au along with secondary electron image of rGO-Au-ZnO NPs hybrid are given in Fig.7.6c-e and the mapped elements are represented in various colours. The secondary electron and backscattered electron images of rGO-ZnO NRs-Au NPs are given in figure 7.6f and 7.6g. Au NPs appear as bright spots and interspersed with ZnO and rGO layers in backscattered image (Fig.7.6g). The Au NPs are aggregated in some regions and are distributed non-uniformly on the surface of ZnO as well as rGO layers.
HRTEM has been performed to study rGO-ZnO and Au-ZnO interfaces with rGO layers and depicted in figure 7.7. Fig. 7.7a shows the shape of ZnO NPs synthesised by solution phase method in the absence of rGO. The NPs are aggregated, and forms elongated features. HRTEM image of individual ZnO NPs show d spacings of 2.8 Å and 2.6 Å corresponding to (100) and (002) lattice planes of wurtzite ZnO, respectively.
Figure 7.7. HRTEM images of as synthesised ZnO hybrids (a) ZnO NPs by solution phase method (b) High resolution image of ZnO NPs in (a) showing lattice fringes of ZnO. The inset shows FFT of HRTEM image. (c) rGO–ZnO NPs obtained by solution
route (d) HREM image of ZnO NPs on rGO (e) rGO–Au–ZnO NPs prepared by solution route. (f) HREM images of (e) showing the lattice planes of Au NPs and ZnO NPs on rGO and also Au–ZnO interfaces with rGO can be seen. The inset shows FFT of the marked Au NP region (g) rGO–ZnO NRs obtained by hydrothermal route (h) HREM image of ZnO nanorods on rGO. The inset gives FFT of the marked region. The FFT shown in the inset give reflections corresponding to $d_{100}$, $d_{002}$, and $d_{101}$. Fig. 7.7c shows isolated ZnO NPs on rGO for rGO-ZnO NPs obtained by solution phase method and Fig.7.7d shows the lattice planes of ZnO NPs corresponding to 2.8 Å (100) and 2.7 Å (112) planes. Fig. 7.7e displays TEM image of rGO-Au-ZnO NPs hybrid. The NPs are embedded in the rGO layers, and HREM image (Fig.7.7f) differentiates Au NPs and ZnO NPs clearly. Au NPs appear dark compared to ZnO in the bright field TEM imaging due to the higher scattering coefficient. Fig. 7.7f shows HREM image of a single Au NP along with ZnO NPs embedded in rGO layers. The lattice planes are corresponding to (111) and (200) plane with multiple domains belonging to polycrystalline FCC structure of Au and the lattice planes indicated in Fig. 7.7f correspond to (110), (101) planes of ZnO. FFT of the selected region of Au NPs (Fig.7.7f inset) also confirms the observation. The lattice fringes of ZnO NPs correspond to (100) (2.8 Å) and (112) (2.8 Å) in Fig.7.7f. Fig.7.7g displays the TEM image of rGO-ZnO NRs prepared by hydrothermal method. ZnO NRs are embedded in the rGO film, and HREM image (Fig. 7.7h) shows lattice fringes with 2.6 Å (002) and 2.7 Å (112) of ZnO. (002) planes are majorly seen along (100-c-axis) for nanorods. FFT given in the inset of Fig. 7.7h gives the reflections corresponding to (110), (100), (112), (002) and (101) lattice planes of ZnO.

7.4 Photocatalysis

The potential application of degradation of organic pollutants in the aqueous phase is a well-known application of many semiconducting NPs. ZnO NPs has been widely used as a photocatalyst for organic dye degradation in water being a non-toxic, most abundant and inexpensive material. The photocatalytic efficiencies of as-prepared composites were
Figure 7.8. Time evolution of UV-visible spectra of 40 µM (19 ppm) solution of RhB dye in the presence of various catalysts when irradiated with 365 nm light of intensity 110 mW cm$^{-2}$.

evaluated by aqueous phase degradation of organic dye rhodamine B (RhB). The photocatalytic effect depends primarily on the shape of the NPs, synthesis method, surface properties and crystallinity of the semiconducting material. The photocatalytic degradation of RhB under UV light was used to evaluate photocatalytic activities of as-synthesized ZnO NPs, rGO-ZnO NPs, rGO-Au-ZnO NPs (solution based) and rGO-ZnO NRs, rGO-Au-ZnO NRs (hydrothermal) composites are shown in figure 7.8. It is clearly

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seen that the photodegradation by as-synthesized rGO-ZnO composites and rGO-Au-ZnO composites are more efficient than by bare ZnO NPs. To study th catalytic rates, \( C_t/C_0 \) vs. irradiation time \((t)\) is plotted and shown in figure 7.8, where \( C_t \) is RhB concentration at a given time during the UV light irradiation and \( C_0 \) is RhB concentration after overnight equilibration with the catalyst before irradiation. From the plots, it is clearly seen that the photodegradation rates of as-synthesised hybrids follow the order rGO-Au-ZnO NPs >

Figure 7.9. Kinetics of 40 \( \mu \)M RB dye degradation a) in the absence and presence of different catalysts (10 mg) b) degradation efficiencies of various catalysts for RhB dye till 40 min irradiation time c) kinetics of RhB dye degradation at different UV light intensities for rGO-ZnO NR composites d) variation of observed rate constant with light intensities.

rGO-ZnO NPs > rGO-ZnO NRs-Au NPs > rGO-ZnO NRs > bare ZnO NPs. Earlier reports show that the dye degradation kinetics follows the pseudo first order kinetics
derived from Langmuir-Hinshelwood mechanism (51, 52) for low reactant concentration. Thus, using the following equation for 1st order kinetics,

\[ C_t = C_0 e^{-K_{obs} t} \]  

The plots in Fig. 7.9a are fitted with the above equation, and the values of \( K_{obs} \) for various photocatalysts are 0.065 min\(^{-1}\) (rGO-Au-ZnO NPs), 0.046 min\(^{-1}\) (rGO-ZnO NPs), 0.039 min\(^{-1}\) (rGO-ZnO NRs-Au NPs), 0.033 min\(^{-1}\) (rGO-ZnO NRs) and 0.0135 min\(^{-1}\) (bare ZnO NPs). So rGO-Au-ZnO-NPs shows 5 times faster degradation than bare ZnO NPs and 1.5 times faster than rGO-ZnO NPs and 2 times faster than rGO-ZnO NRs. The degradation efficiency of as-synthesized hybrids is calculated by employing the given expression,

\[ \text{Degradation efficiency} = \frac{C_0 - C_t}{C_0} \times 100 \]  

Degradation efficiency of hybrids is compared and depicted in Fig. 7.9b. At 40 min, the degradation efficiency is 96 % for rGO-Au-ZnO NPs hybrid while it is 56 % for rGO-ZnO NRs-Au NPs. rGO-ZnO NRs-Au NPs have shown initially very slow degradation due to the coverage of Au NPs and poor interfacing between rGO, Au, and ZnO nanostructures. rGO-ZnO NPs shows 84 % degradation while rGO-ZnO NRs shows only 67 % and the bare ZnO NPs shows 36% degradation at 40 min. During the initial 20 min degradation, the degradation % of RhB with rGO-ZnO NRs is slightly higher than the rGO-ZnO NPs. To compare with very recent report that presents the methyl orange degradation by rGO-ZnO-Ag NPs, the reported degradation efficiency is only 94 % for 68 min and in another case of RhB, complete degradation using rGO-ZnO NPs is achieved in 60 min.(53) The kinetics of RhB photodegradation is also studied by varying the UV light power or intensity for the catalyst, rGO-ZnO NRs, without changing other experimental parameters (Fig. 7.9c). The observed rate constants (\( k_{obs} \)) increase with light intensity (I)
as $k_{obs} = I^{-0.74}$ (Fig. 7.9d). In the earlier reports, the rate varies as the square root of intensity at higher light intensities and in some cases, it is between 0.5 and 1.\(^{54}\) Linear variation has been observed at sufficiently low intensities.\(^{55}\)

rGO acts as an excellent adsorbent for organic pollutants like activated carbon, and also, it serves as a medium to charge transport to reduce the electron-hole recombination rates. During photodegradation studies of RhB dye using ZnO hybrids, we have noticed that RhB dye molecules get adsorbed on rGO based ZnO hybrids more than that for bare ZnO NPs. The absorbance maxima of RhB decreases after overnight equilibration with the catalyst in the dark (taken as $C_0$). Therefore, for rGO-ZnO NRs, the initial concentration of 40 µM RhB solution has reduced to 35 µM after overnight equilibration in the dark. The decrease in concentration of RhB dye increases with the increase in rGO content in the catalyst. The adsorption capacity of the hybrids has been calculated from the below expression and depicted in figure 7.10.

$$Q = \frac{(C_{\text{initial}} - C_0)V}{m} \quad \text{equation 19}$$

![Figure 7.10. The ratio of equilibrium concentration to initial concentration for various catalysts.](image-url)
where $Q$ is the adsorption capacity at equilibrium (mg g$^{-1}$), $V$ is the volume of solution and $m$ is the mass of the catalyst. $C_{\text{initial}}$ and $C_0$ are defined as above and expressed in mg L$^{-1}$. The adsorption capacity of rGO-ZnO NPs is 37.7 mg g$^{-1}$ and for rGO-Au-ZnO NPs, rGO-ZnO NRs-Au NPs, rGO-ZnO NRs, and bare ZnO NPs is 23.8, 13, 11.9 and 6.4 mg g$^{-1}$, respectively. The adsorption capacity of rGO-ZnO NPs is comparable with an earlier report showing the absorption capacity of 32.6 mg g$^{-1}$ for rGO-ZnO composite.\(^{(56)}\) It is noticeable that though the rGO-ZnO NPs have the highest adsorption capacity, they have a lower degradation rate than the rGO-Au-ZnO NPs, which is discussed below.

### 7.5 Discussion

When ZnO materials are excited with UV light, electrons (conduction band) - holes (valence band) pairs are generated, which are responsible for the photocatalytic effect. The efficiency of ZnO photocatalyst has been improved by combining with rGO and rGO-Au NPs.\(^{(57-59)}\) The enhancement in photocatalytic rates due to the charge transfer between the ZnO to the other components of the hybrid leads to the suppression of e-h pairs in the photoexcited ZnO. In the case of rGO-ZnO and rGO-Au-ZnO composites, the rGO and Au (gold) act as reservoirs for photo-generated electrons and facilitates the transfer of photo-induced electrons from ZnO to rGO and Au and inhibit the recombination of photogenerated electron-hole pairs so that the lifetime of the electron and hole pairs have been increased, which are available for reaction with hydroxyl ions and generating hydroxyl and superoxide radicle ions that are responsible for degradation of RhB dye molecules. Mainly, the enhancement of photocatalysis in these composites is due to the synergic effect.

The rGO can act as a photosensitizer and photocatalyst by itself when rGO irradiation with UV light to generate electron-hole pairs. The addition of rGO to ZnO can improve the photocatalytic performance of ZnO, mainly due to the three reasons, (1) rGO
Figure 7.11. a) PL spectra of rGO-ZnO NRs synthesised by hydrothermal route before and after removing rGO by sintering in air b) FESEM image of ZnO NRS after removing rGO c) Time evolution of UV-visible spectra of 40 µM (19 ppm) solution of RhB dye in the presence of ZnO NRs (7.2 mg) catalyst when irradiated with 365 nm light of intensity 110 mW cm⁻².

can provide high surface area to adsorb organic dye (interaction between the graphene aromatic carbons and aromatic molecules of organic dye by π-π interaction) (2) Good conductor to transport photogenerated electrons (3) It can increase the absorption of light. Various possible charge transfer mechanisms with irradiation of UV light are (1) excited state electron transfer from ZnO conduction band and defect level to rGO and Au (2) excited state electron transfer from RhB conduction band to ZnO, rGO and Au energy levels (3) surface plasmon enhanced electron transfer from Au levels to the ZnO and rGO. The last two mechanisms need to be considered for the visible light based catalysis. Here, we have employed UV irradiation for photocatalysis of RhB dye. So, the first mechanism is more plausible. In situ synthesis of hybrids gives the proper physical interface between the components, which facilitates the band bending and charge transfer. The nature of charge transfer is reflected in PL spectra of rGO-ZnO hybrids as
quenching of band-edge peaks at 380 nm and visible defect emission (Fig. 7.4). Here, rGO acts as an acceptor and 2D conductor for photoexcited electrons from ZnO conduction band and defect levels. We have removed rGO content selectively from rGO-ZnO NRs by sintering at 300°C in air and subjected them to PL and photocatalysis (Fig. 7.11). The PL spectra of ZnO NRs display a high intense band edge and visible emissions similar to that of bare ZnO NPs. The morphology of ZnO NRs is not changed after sintering. The photodegradation rate \( k_{obs} = 0.0021 \text{ min}^{-1} \) has become very slow; one order less than the rGO-ZnO NRs hybrid. This again proves that the charge carriers generated when ZnO is irradiated with photons of energy equal to or greater than the band gap are separated efficiently in the presence of rGO. The charge carriers could be combined with the absorbed energy dissipated as heat, or they can migrate to the surface of the ZnO particle. (60, 61) In the presence of rGO or Au NPs systems, due to the lower Fermi level energy of rGO or Au NPs, the excited electrons in ZnO system preferentially transfer to the rGO or Au NPs and leaving the holes on the surface of the ZnO component.

\[
ZnO + h\nu \rightarrow ZnO(e^- CB + h^+ VB) \quad \ldots \ldots \quad 20
\]

\[
ZnO (e^-) + \text{rGO or Au NPs} \rightarrow ZnO + \text{rGO or Au NPs} (e^-) \ldots \ldots \quad 21
\]

The holes can react with the surface bound hydroxyl groups (OH⁻) and adsorbed water molecules to form hydroxyl radicals (OH⁻).

\[
h^+ + OH^- \rightarrow OH^- \quad \ldots \ldots \quad 22
\]

\[
h^+ + H_2O \rightarrow OH^- + H^+ \quad \ldots \ldots \quad 23
\]

The presence of oxygen vacancies in the ZnO particle thwart the recombination of e⁻-h⁺ pairs by trapping electron through the formation of superoxide ions and maintaining
electron neutrality within the ZnO nanoparticle. The final products of this reaction are commonly hydroxyl radicals (OH) and hydroperoxyl radicals (HO$_2$).(60, 61)

\[ 2O_2^- + H^+ + h^+ \rightarrow 2OH + O_2 \quad \ldots \ldots \ldots 24 \]

\[ 2O_2^- + H^+ + h^+ \rightarrow HO_2^- \quad \ldots \ldots \ldots 25 \]

The hydroxyl radicals are known to be potent, haphazard oxidizing agents and during the photocatalytic process, they can react with the organic dye compounds and ensuing in degradation of dye molecules. The overall oxidative and reductive reaction schemes of photodegradation of organic dye compounds are shown in the following equations.(60, 61)

**Oxidative reaction:**

\[ h^+ + \text{Organic dye} \rightarrow (\text{Intermediates}) \rightarrow CO_2 + H_2O \quad \ldots \ldots \ldots 26 \]

\[ h^+ + H_2O \rightarrow OH^- + H^+ \quad \ldots \ldots \ldots 27 \]

**Reductive reaction:**

\[ OH^- + \text{Organic dye} \rightarrow (\text{Intermediates}) \rightarrow CO_2 + H_2O \quad \ldots \ldots \ldots 28 \]

The mechanism of photocatalytic based dye degradation by identification of intermediate products is the best way to explain reaction pathway. The schematic way of photodegradation of RhB dye in the presence of the photocatalyst is given in figure 7.12. RhB dye is stable in the aqueous solutions under the UV and visible light radiation in the absence of photocatalyst. According to the earlier reports, RhB dye adsorb on the surface of photocatalyst through positively charged N-diethyl amino group. Under UV light irradiation, the degradation occurs via two pathways; one is stepwise N-deethylation, and the other is the destruction of the conjugative structure followed by mineralization of organic molecules.
Figure 7.12. Probable reaction pathway for the photocatalytic degradation of RhB dye. (62) rGO-Au-ZnO NPs hybrid shows the highest photocatalytic rate (Fig.7.9) because both rGO, and Au components can participate in the charge separation limiting the e-h recombination. The Au levels offer alternative pathways for transfer of photoexcited electrons from ZnO conduction band. Earlier reports show that the Au nanocore can store
electrons until the equilibration of Fermi level with the ZnO conduction band.\(^{(63)}\) In the case of rGO-ZnO NRs-Au NPs, due to the poor interfacing between the components the photocatalytic rates are initially very slow and after that, the degradation rate is faster. The PL spectra also show that the band edge emission peak is not suppressed significantly and also shows visible emission due to the surface plasmon scattering of Au NPs, which has been utilised by other researchers for visible light photocatalysis. ZnO hybrids synthesised by hydrothermal route display lower photocatalytic rates compared to ZnO hybrids by solution phase method. This is due to lesser suppression of the e-h recombination, which is reflected in PL spectra and also the lower content of rGO to ZnO ratio in the hydrothermally prepared ZnO hybrids. The nanorod morphology of ZnO is also the reason to show low rates compared with NPs. The surface of ZnO NRs has mostly nonpolar facets while in the case of spheroidal NPs contain more polar facets that facilitate the hydroxyl ions adsorption. A schematic charge transfer process is shown in figure 7.13. rGO is an excellent adsorbent for dye molecules, and it can also affect the degradation rates as the rate is proportional to the available adsorption sites and surface.

Figure 7.13. Schematic illustration of the possible charge transfer processes in the rGO-Au-ZnO NP hybrid during the photodegradation process.
coverage according to Langmuir-Hinshelwood mechanisms.\(^{64}\) rGO-ZnO NPs (solution route preparation) having the highest rGO content and accordingly higher adsorption capacity leads to the higher degradation rates. However, the degradation rate is lower than rGO-Au-ZnO NPs. The order of photocatalytic rates of ZnO hybrids is rGO-Au-ZnO NPs > rGO-ZnO NRs-Au NPs > rGO-ZnO NPs > rGO-ZnO NRs > bare ZnO NPs and also the results shows that the photodegradation rates are more influenced by suppression in e-h pair recombination due to charge transfer facilitated by Au and rGO constituents in the ternary hybrid system than a higher surface coverage.

**II. Hybrid films of rGO-metal oxide nanostructures and doped with metal nanoparticles formed at a liquid/liquid interface as reusable SERS substrates for dyes**

7.6 Experimental Details

7.6.1 Materials

Bis(2,4-pentanedionate) zinc monohydrate (Zn(acac)\(_2\)) H\(_2\)O, copper (II) acetylacetonate (Cu(acac)\(_2\)), tin (IV) bis(acetylacetonate) dichloride (Sn(acac)\(_2\)Cl\(_2\)), KOH, absolute Ethanol (99.99%), tetrakis(hydroxymethyl) phosphonium chloride (THPC) (80% aqueous solution), rhodamine 6G, and toluene were purchased from Sigma-Aldrich and used as received without any further purification. Exfoliated graphene oxide (GO) was synthesized from graphite (-300 mesh, Alfa-Aesar) powder employing modified Hummer’s method.\(^{47}\)

7.6.2 Synthesis of rGO-metal oxide nanostructures (rGO-ZnO, rGO-CuO and rGO-SnO\(_2\))

rGO based metal oxide NP hybrid films were prepared by liquid/liquid interface single step method. In this method, 25 mL of toluene containing 30 µmoles of metal acetylacetonate precursor was layered over 25 mL milli-Q water containing 5 mg of GO in a 100 mL beaker. A water/toluene interface with precursors in two phases is obtained,
and then 200 µmoles of KOH with 25 µL of THPC were injected into the aqueous phase with the least disturbance. The whole system was heated at 90 °C in an oil bath for 2 hr. After 1 hr, ultra-thin film of rGO-metal oxide NP hybrid film was observed at the liquid/liquid interface. These films appeared thin and uniform covering the entire interface. They were collected on to desired substrates after the toluene solvent evaporation.

7.6.3 rGO-Ag-ZnO NPs hybrid film

Metal nanoparticle doped rGO-metal oxide films were prepared by introducing metal ions in the organic phase along with metal oxide precursor. In the case of rGO-Ag-ZnO NPs preparation, 25 mL of toluene containing 30 µmoles of Zn(acac)$_2$H$_2$O and 2 mL of 1.5 mM Ag(PPh$_3$)$_4$NO$_3$ solution was poured over 25 mL of milli-Q water containing 5 mg GO. 200 µmoles of KOH and 25 µL of THPC was injected into the aqueous phase with least disturbance to the interface. The whole system was heated at 90°C in an oil bath for 2 hr. After 1 hr, a thin film of rGO-Ag-ZnO NPs was observed at the interface.

7.7 Results and discussion

Fabrication of nanomaterials film at a liquid/liquid interface can be achieved by, self-assembly of preformed colloidal dispersions or in situ reaction at interface followed by the self-assembly.(65, 66) Here, we have employed interfacial hydrolysis reaction for the synthesis of rGO-metal oxide NPs ultrathin films including rGO-ZnO, rGO-CuO, and rGO-SnO$_2$. The method involves taking metal precursor (Zn$^{+2}$, Cu$^{+2}$, and Sn$^{+4}$ acetylacetonate compounds) in organic phase over an aqueous phase containing GO, followed by the addition of alkali (KOH) and THPC (reducing agent) to the aqueous phase. The hydrolysis of metal-organic precursor occurs at the interface and leads to the formation of metal oxide NPs and get anchored on the surface of rGO. GO gets reduced by THPC and diffuses towards the interface and self-assembles due to the capillary forces.
and hydrophobic interactions. rGO can facilitate the nucleation of metal oxide seeds due to the presence of hanging oxygen functional groups. Fig. 7.14 shows the schematic of the reaction process. Multifunctional NPs of metal along with metal oxide on rGO sheets can be synthesized by taking noble metal precursor along with the above reactants wherein THPC can also reduce noble metal ions to metal NPs in situ. Hence, hybrid films of rGO-Ag-ZnO NPs have been obtained by taking silver-triphenyl phosphine and zinc acetylacetonate in the organic phase over GO, KOH, and THPC in the aqueous phase.

Figure 7.14. Schematic of the synthetic process to obtain rGO-metal oxide NP hybrid films at the interface (single-step process).

The in situ reaction takes place at the interface and followed by the self-assembly of metal nanoparticles and metal oxide nanostructures and rGO at the interface. The crystal structure of as-synthesized hybrid films was studied by XRD and is depicted in fig. 7.15. As recorded XRD patterns of ZnO, rGO-ZnO, and rGO-Ag-ZnO confirms that ZnO NPs are crystalline and the peaks at 31.8° (100), 34.4° (002), 36.3° (101), 47.6° (102), 56.7° (110), 62.9° (103), 66.4° (200), 67.9° (112), 69.2° (201), 72.7° (004) and 77° (202), confirms the formation of hexagonal wurtzite structure of ZnO (Fig.7.15a) (PCPDF No. 89-0511). rGO-Ag-ZnO shows additional reflections corresponding to FCC Ag at 38.16° (111) and 44.26° (322) along with that of ZnO. rGO-CuO (Fig.7.15b) shows very low intense CuO reflections at 35.46° (002), 35.56° (-111), 38.76° (111), 38.93° (200), 48.70°
(−202) and 56.78° (021), corresponding to monoclinic crystal structure (PCPDF No. 89-5899). In the case of rGO-SnO2 (Fig. 7.15b), reflections due to SnO2 are seen at 33.87° (101), 37.956° (200), 51.77° (211) and 64.74° (112) corresponding to the tetragonal crystal structure (PCPDF No. 88-0287). The broad diffraction patterns indicate the formation of extremely small SnO2 particles on rGO layer. The optical properties of as-synthesized hybrid films at the interface were studied by UV-visible absorption, photoluminescence spectra and are given in fig. 7.16. The excitonic absorption peak of ZnO arising from band gap transitions appear at 355-360 nm in the case of rGO-ZnO and rGO-Ag-ZnO. rGO-Ag-ZnO hybrid films also display a broad absorption at 400 nm due to the surface plasmon resonance absorption of Ag NPs (Fig. 7.16a). rGO-CuO hybrid film shows a significant absorption at 290-360 nm, and rGO-SnO2 shows a broad absorption at 550 nm corresponding to band edge absorption (band edge absorption of bulk CuO is expected at 380 nm (3.25 eV) and the band edge absorption of bulk SnO2 at 345 (3.6eV). The band gap narrowing of SnO2 is due to the presence of higher concentration of oxygen vacancies, which is reflected in PL spectra as intense visible emission. In all hybrid films, the absorption at 263 nm has seen due to π-π* transition of sp² carbons of rGO.

![Figure 7.15. XRD patterns of rGO-metal oxide hybrid films synthesized at a liquid/liquid interface (a) rGO-ZnO and rGO-Ag-ZnO (b) rGO-CuO and rGO-SnO2 NPs hybrid films.](image-url)
Figure 7.16. (a) UV-visible absorption spectra (b) and (c) Room temperature photoluminescence (PL) spectra of rGO based metal oxide hybrid films, rGO-ZnO, rGO-Ag-ZnO, rGO-SnO$_2$, and rGO-CuO prepared at a liquid/liquid interface.

The room temperature PL spectra of as-synthesized hybrid films are given in figure 7.16b,c. Generally in ZnO, the visible range emission composed of green, blue, yellow luminescence arises due to the presence of a variety of oxygen vacancies. (67) Jennette et al. have reported that only three charge states of oxygen vacancies are possible within the various energy states of ZnO. (68) The origin of these green, blue and yellow peaks can be attributed to the presence of interband (trapped states or defect levels consisting zinc interstitials and oxygen vacancies) energy levels in the ZnO particles (Fig.7.17). The possible electron recombinations and trapstates or defect states present in the ZnO particles are depicted in figure 7.17.
We have also observed a broad visible luminescence in the range of 350 to 600 nm. The emission at 380 nm comes from the electron-hole recombination in ZnO. The visible region consists of peaks around 408 nm, 440 nm (violet, blue emission), 490 nm (blue emission) and 532 nm (green, yellow emission). The intensity of PL emission is seen quenched for rGO-ZnO and rGO-Ag-ZnO NPs film compared with that of bare ZnO due to the presence of rGO and Ag NPs facilitating charge transfer from ZnO energy levels to the rGO or Ag and reduces recombination rates. Hence, we have observed reduced PL intensity. We have also found low intense NIR PL spectra for ZnO and rGO-ZnO hybrids in the range of 750-900 and may be ascribed to the second order diffraction of UV luminescence. The NIR emission possibly arises from active UV emission of ZnO and also different types of oxygen defects present in the ZnO. The PL spectra of rGO-SnO$_2$ show a broad emission from 360-600 nm similar to the case of the rGO-ZnO system. Emission due to electron-hole recombination appears at 375 nm, and visible emission arises at 420 nm, 450 nm and 530 nm due to oxygen vacancies. Fig. 7.16c shows the PL spectra of CuO NPs on the rGO sheets. The PL spectra show UV emission peaks.
at 290 nm, 392 nm and a visible emission peak at 560 nm (weak yellow emission). The peak around 290 nm is attributed to electron-hole recombination emission (band edge emission) and the peaks around 392 (violet emission) is attributed to near band edge recombinations while the very weak emission at 560 nm is contributed by the surface defects of CuO. (70-72)

The surface morphology and topography of as-synthesized hybrid films were examined by FESEM, and the images are shown in fig. 7.18. ZnO shows hexagonal disk shapes in the rGO-ZnO hybrid film. They are stacked over one another to form hexagonal cylinders and interspersed with rGO sheets. The length and width of these cylinders are vastly polydisperse. A higher magnified image of one of these cylinders shown in the inset has 180 nm length and 80 nm width. Some of the ZnO small hexagonal cylinders on rGO sheets resemble the Indian musical instrument, Damaru (musical instrument of Lord Shiva). The morphology of rGO-CuO shown in fig.7.18b consists of spiky features of CuO that appear as splinters embedded in CuO film and the rGO layer is present beneath the CuO layer. A magnified image of CuO film in the inset shows the granular thin film with tiny CuO NPs. In the case of rGO-SnO2 (Fig.7.18c) hybrid film, SnO2 shows core-shell spheres along with ultra-small NPs on the rGO layer. The core-shell SnO2 spheres are around µm size and consist of tiny SnO2 NPs and wrapped by rGO sheets. A high-resolution image of the thinner area of rGO-SnO2 shown in fig.7.18d, reveals SnO2 NPs with average size of < 5 nm interspersed with rGO layers. The particles size distribution of metal oxide NPs along with metal NPs on rGO histograms are given in figure 7.20.

The morphology of ZnO in the rGO-Ag-ZnO exhibit a mixture of rice shaped NPs and hexagonal cylinders (fig.7.18e). With the introduction of a small amount of Ag+ ions (3 µmoles) in the rGO-ZnO reaction system, a different morphology of ZnO, rice shaped NPs are observed along with hexagonal NPs for rGO-Ag-ZnO (Fig.7.18e). Inset of
Figure 7.18. FESEM images of rGO-metal oxide hybrid films synthesised at the liquid/liquid interface a) rGO-ZnO; inset shows high magnification image of hexagonal rGO layer.

b) CuO spikes and sheet.

c) SnO$_2$ NPs (spheres).

d) SnO$_2$ NPs (ultra small).

e) rGO layer.

f) Ag NPs (Bright spots).
cylinders b) rGO-CuO; inset shows zoomed in view of the CuO sheet c) rGO-SnO$_2$; inset gives high magnification image of core-shell SnO$_2$@rGO spheres d) high magnification image of the thinner area of rGO-SnO$_2$ marked in (c). e) rGO-Ag-ZnO; inset shows rice shaped ZnO NPs f) backscattered electron image of the rGO-Ag-ZnO NPs hybrid film.

Figure 7.19. FESEM images of (a) ZnO NPs film (b) Ag-ZnO NPs film synthesized employing liquid/liquid interface single step method.

fig.7.18e display a region of rice shaped ZnO NPs. the change in morphology of ZnO NPs can be explained due to the presence of Ag$^+$ ions in the reaction solution. Ag$^+$ ions are known to influence the morphology of ZnO.(73) However, we believe that Ag$^+$ loading, in this case, is not sufficient enough to bring out a morphology change of the whole system, and hence, a mixture of rice and hexagonal ZnO is obtained. We observed rice shaped ZnO morphology for Ag-ZnO and hexagonal cylinders for bare ZnO films in the absence of rGO, in an independent preparation (Fig.7.19a,b). In order to show the presence of Ag NPs in rGO-Ag-ZnO films, backscattered SEM image is presented in Fig. 7.18f. the bright spots corresponding to Ag NPs can be clearly seen among ZnO nanostructures supported on rGO. The coverage of Ag NPs is found to be sparse, and the sizes are highly polydisperse, ranging from 5-30 nm.

High-resolution TEM was performed to study the crystallinity and morphology of metal oxide nanostructures in more detail. HREM images of different hybrid films are
Figure 7.20. Particles size distribution of various hybrid films NPs shown a) & b) displays the length and width of ZnO hexagonal cylinders c) Ag NPs size in rGO-Ag-ZnO hybrid film d) & e) CuO splinters features length and width and f) & g) SnO$_2$ core-shell spheres size and ultra small SnO$_2$ particles size, respectively.

given in figure 7.21. Figure 7.21a shows HREM image of rGO-Ag-ZnO film. In fig. 7.21a, rice shaped ZnO NP can be seen at the edge of the film with $d_{002}$ (2.6 Å) and $d_{101}$ (2.5 Å) lattice planes and hexagonal carbon network of the rGO layer is clearly seen around rice shaped ZnO NP at the film edges (inset). Ag NPs are also observed along with ZnO NPs and show lattice spacing 2.09 Å and 2.4 Å corresponding to $d_{200}$ and $d_{111}$ planes. Top inset of fig.7.21a shows the SAED of the rGO-Ag-ZnO hybrid film with reflections corresponding to (100), (002), (110) planes of ZnO and (200) of Ag NPs. SnO$_2$ spheres warped with rGO layers are clearly seen in the TEM images of rGO-SnO$_2$ shown in fig.7.21b. A highly magnified image of the marked region is given in the inset, where the edge of the core-shell SnO$_2$ spheres is broken and reveals that the spheres are formed by the aggregation of ultra-small SnO$_2$NPs. An HREM image of SnO$_2$ NP is also
Figure 7.21. HRTEM images of as-synthesized hybrid films a) rGO-Ag-ZnO film, high-resolution images of marked regions corresponding to Ag NPs and rGO layer (inset) and SAED pattern (inset) b) rGO-SnO$_2$ film, core-shell SnO$_2$@ rGO spheres, high-resolution images of marked area of a sphere and SnO$_2$ NPs (inset), SAED pattern (inset) c) rGO-CuO film, SAED pattern (inset) d) High resolution image of the tip of a nanosplinter structures in (c) showing CuO sheet covered by rGO layer; lattice fringes of CuO (inset). given in the inset, which shows 3.38 Å related to $d_{110}$ lattice plane. SAED show rings corresponding to (112), (211), (101), (110) planes. Fig.7.21c displays the splinter features of CuO embedded in CuO film for rGO-CuO hybrid film. SAED patterns show reflections corresponding to lattice planes of monoclinic CuO, (110), (111), (-202), (021) and (022). An HREM image of the tip of a CuO splinter is given in Fig.7.21d and shows
CuO sheets embedded in rGO layers. The lattice fringes indicate $d_{111}$ (2.39 Å) plane along the long axis of sheet.

### 7.8 SERS studies

To investigate the potential application of as-synthesized hybrid films as SERS substrates, we examined the Raman spectra of R6G, a fluorescent analyte as the probe molecule. Fig. 7.22 shows the Raman spectra of 1 mM R6G adsorbed on the rGO-metal oxide hybrid films supported on glass substrates. The characteristic vibration peaks of R6G are seen displayed in the fingerprint region, and the assignments of the peaks are presented in the given table 7.2. When compared with R6G peaks on ZnO without rGO, all the hybrid

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**Figure 7.22.** rGO-metal oxide NPs and metal NPs doped hybrid films as SERS substrates a) SERS for 1 mM R6G dye on rGO-metal oxide hybrid films b) EF factor comparison for various hybrid films c) SERS for different concentrations of R6G dye on rGO-Ag-ZnO hybrid film d) Intensity of 618 cm$^{-1}$ for various R6G concentrations on rGO-Ag-ZnO hybrid film obtained from (c).
films have shown enhancement in Raman intensities with a slight inhibition in the fluorescence background. The improvement in the intensity of Raman peaks due to the charge transfer between the adsorbed dye molecules and metal oxides. The primary mechanisms for photoinduced charge transfer in the above systems are (1) excitation of electrons to defect levels (commonly observed in metal oxides) by visible light, which is employed for Raman scattering and further transferred to LUMO of molecules (2) excitation of electrons in dye HOMO-LUMO levels by the visible light and further moved to CB of ZnO levels in the case of fluorescent dye molecules as analytes. In the case of bare ZnO films, R6G Raman peaks slightly enhanced, and the broad fluorescence background from the dye masks the enhancement effect. When ZnO is combined with rGO, the local electric field generated due to the dipole moment contribution from the remnant oxygen functional groups of rGO adds to the chemical enhancement effect of ZnO NPs(75) and also causes fluorescence quenching. A similar phenomenon is seen in the case of rGO-CuO and rGO-SnO2 hybrid films. Hence, the SERS effect by rGO-metal oxide hybrid films is due to the synergic effect of charge transfer between metal oxide NPs, R6G, and rGO layers and also molecular resonance of R6G.
The enhancement factor (EF) values of R6G on as synthesized hybrid films have been calculated from the most intense peak (618 cm\(^{-1}\)) of R6G as follows.

\[
EF = \frac{I_{\text{SERS}}}{I_{\text{bulk}}} \times \frac{N_{\text{bulk}}}{N_{\text{SERS}}} \quad \ldots \ldots \ldots \quad 8
\]

where \(N_{\text{bulk}}\) is the number of the probe molecules under laser illumination in the bulk sample and \(N_{\text{SERS}}\) is the number of the molecules investigated on the hybrid nanoparticle substrate respectively. \(I_{\text{SERS}}\) and \(I_{\text{bulk}}\) are the vibrational intensities of R6G on the hybrid substrate and bulk sample respectively for the same Raman band. Here, the most prominent peak 618 cm\(^{-1}\) of R6G has been chosen to calculate EF with excitation of 532 nm laser. Since neat R6G is highly fluorescent, 1 mM R6G aqueous solution has been analyzed for bulk Raman spectra. 1 mM R6G aqueous solution on a glass substrate has been considered for bulk Raman spectra.

\(N_{\text{bulk}}\) has been calculated using following equation

\[
N_{\text{bulk}} = \frac{Ah\rho}{m} \quad \ldots \ldots \ldots \quad 9
\]

Where \(A\) is the area of the laser spot (1.53 \(\mu\)m\(^2\)), \(h\) is the laser penetration depth (10.5 \(\mu\)m for 532 nm), \(\rho\) (1.26 g/cm\(^3\)) and \(m\) (479.02 g/mol) are the density and molecular weight of the R6G analyte, respectively. The calculated value of \(N_{\text{bulk}}\) is \(\sim 4.2 \times 10^{-14}\) moles. Park and co-workers\(^{(76)}\) have given the procedure for calculating \(N_{\text{SERS}}\). With the help of laser spot size, the number of molecules of R6G present under laser illumination can be estimated by taking the sampling area and the number of moles into account as

\[
N_{\text{SERS}} = \left( \frac{\text{Concentration (moles)}}{\pi (3 \text{ mm})^2} \right) \times [\pi (0.7 \mu\text{m})^2] \quad \ldots \ldots 10
\]

The concentration of R6G adsorbed on rGO-ZnO thin film was \(1 \times 10^{-8}\) moles (for 10 \(\mu\)L of 1mM R6G).
The calculated $N_{SERS}$ value is $\sim 5.4 \times 10^{-16}$ mol.

$N_{Bulk}$ value is is $\sim 4.2 \times 10^{-14}$ mol

$I_{SERS}$ value is 2671 for rGO-ZnO (Intensity of 618 cm$^{-1}$ peak of R6G)

$I_{Bulk}$ value is 500 (Intensity of 618 cm$^{-1}$ peak of R6G bulk)

$$EF = \frac{2671}{500} \times \frac{4.2 \times 10^{-14}}{5.4 \times 10^{-16}}$$

EF is $\sim 4.15 \times 10^2$ for rGO-ZnO hybrid NP substrate

$I_{SERS}$ values for EF calculation in the case of rGO-CuO and rGO-SnO$_2$ films are taken as 4067, 2085 and for 10 $\mu$L of 1 mM R6G dye.

A comparison of EF values for various hybrid films is given in Fig. 7.22b. As seen from SERS spectra, EF for rGO-ZnO ($4.2 \times 10^2$) is one order higher than bare ZnO and among rGO-metal oxide systems studied in this work, rGO-SnO$_2$ exhibit slightly lower EF ($3.2 \times 10^5$). For the rGO-SnO$_2$ system, it is evident that the NP size is tiny (< 5 nm) compared to ZnO and CuO. For very small particles, a strong quantization causes weak vibronic coupling resulting in less intensity of Raman spectra. EF values follow the order rGO-Ag-ZnO > rGO-CuO > rGO-ZnO > rGO-SnO$_2$ > bare ZnO. Generally, Raman enhancements due to chemical or charge transfer effect are moderate of the order 10-100, while electromagnetic enhancement is enormous of the order $10^6$. In this study, rGO-ZnO NPs system with relatively good EF is chosen to be doped with Ag NPs (3 $\mu$mol of Ag$^+$ precursor) for further enhancement in EF and rGO-Ag-ZnO hybrid films are explored as SERS substrates. The presence of Ag NPs in the rGO-ZnO system drastically improves the Raman scattering from adsorbed R6G dye. The calculated EF for the rGO-Ag-ZnO film (1 mM R6G) ($1 \times 10^3$), is one order higher than the rGO-metal oxides films ($4.2 \times 10^2$) (Fig. 7.22b). EF was calculated following the above formulae, intensity of 618 cm$^{-1}$ peak is taken as 8425. The detection sensitivity of the rGO-Ag-ZnO hybrid film is studied for various concentrations of R6G (Fig. 7.22c).
The intensity of 618 cm\(^{-1}\) peaks of different concentrations of R6G on rGO-Ag-ZnO films is depicted in Fig. 7.22d and detection up to 10 \(\mu\)M is achieved with an EF of \(10^4\). For the EF calculation of 10 \(\mu\)M R6G solution on rGO-Ag-ZnO hybrid film, the concentration of R6G adsorbed is taken as \(1 \times 10^{-10}\) moles (for 10 \(\mu\)L). The calculated \(N_{SERS}\) value is \(5.4 \times 10^{-18}\) mol. \(N_{Bulk}\) value is \(4.2 \times 10^{-14}\) mol and \(I_{SERS}\) value is 602 (618 cm\(^{-1}\) peak for 10 \(\mu\)M R6G). Substituting all the values, \(EF = (602 / 500) \times (4.2 \times 10^{-14} / 5.4 \times 10^{-18})\) gives EF as \(\sim 1 \times 10^4\) for rGO-Ag-ZnO films. So, the introduction of a small percentage of Ag NPs drastically improves EF and detection sensitivity of molecules owing to the electromagnetic field effect from Ag surface plasmons.
We have studied the reusability of as-synthesized hybrid films as SERS substrates for fluorescent analytes. Degradation of analytes occurs by photocatalytic nature of metal oxides. Fig.7.23 shows the SERS spectra of R6G, before and after photodegradation for various hybrid films. Photodegradation is performed by subjecting 1 mM R6G adsorbed on to the hybrid films wetted with water, to UV light. After 30-40 min of UV light irradiation, the R6G dye signatures vanished, and only a broad background is observed. The reusability is proved with respect SERS of another dye, methylene blue (MB), adsorbed on the hybrid films after degradation of R6G dye. The vibrations of MB are clearly seen in the Raman spectra, and as expected, the enhancement for most vibrational signatures is improved in the case of rGO-Ag-ZnO NPs hybrid film. The assignments of MB vibrational peaks are given in Table 7.3.

Figure 7.24 explains the charge transfer process across the hybrid films and adsorbed dye molecules. The R6G molecules absorb the 532 nm laser light and get excited, the excited electrons transfer from CB of R6G to the ZnO CB followed to the rGO. Due to this charge transfer, the fluorescence of dyes could be suppressed. Reusable
substrates based Ag-ZnO nanostructures have been reported earlier. However, coupling Ag-ZnO by rGO layers can be more beneficial in terms of efficient adsorption of dye molecules and enhanced charge separation promoting faster degradation kinetics. This has been demonstrated in our earlier studies with respect to rGO-ZnO and rGO-Au-ZnO systems.

Figure 7.24. Photographs of rGO-Ag-ZnO NPs hybrid films on a quartz substrate used as reusable SERS substrates and probable mechanism for the fluorescence quenching.

III. Synthesis and characterization of Ag₂S and rGO-Ag₂S thin films at a liquid/liquid interface

7.9 Experimental details

7.9.1 Materials

Exfoliated graphene oxide was prepared from highly oriented pyrolytic graphite flakes (ZYH grade, Momentive performance) employing modified Hummers method. The graphene oxide (GO) dispersion was purified using 0.2 μm pore size nylon filter paper, sonicated and a standard solution was prepared for further use. The metal precursor,
Ag(PPh₃)₄NO₃ was made in our laboratory and Na₂S is used as the sulphur source for preparation of rGO-Ag₂S nanocomposite film. Tetrakis(hydroxymethyl)phosphonium chloride (THPC) (80% aqueous solution, Aldrich) was used as the reducing agent when required.

### 7.9.2 Synthesis of silver sulfide and rGO-Silver Sulfide NP films

10 mL of 1.5 mM Ag(PPh₃)₄NO₃ to was added to 25 mL toluene solution and poured over 25 mL of milli-Q water containing 7.5 μmoles of Na₂S. The system was heated in an oil bath at 90 °C and after 1 hr a black Ag₂S NPs film was observed at the water/toluene interface. The film was collected on various substrates such as quartz, Si and SiO₂ substrates for further characterization.

The rGO-Ag₂S nanocomposite was prepared by adopting liquid/liquid interface in one step synthesis or a two-step reaction sequence. In one step synthesis (Fig.7.25a), GO was taken in aqueous phase along with the sulphur source and the metal precursor was taken in the toluene phase. In a typical reaction, rGO -Ag₂S nanocomposite was prepared by taking 25 mL of toluene along with 10 mL of 1.5 mM Ag(PPh₃)₄NO₃ toluene solution over 25 mL of milli-Q water containing 0.01 mg mL⁻¹ GO and 7.5 μmoles of Na₂S. The whole system was heated at 90 °C in an oil bath for 1 hour, a thin film of the hybrid material was observed at the interface.

In the two-step method (Fig.7.25b), the rGO film was formed initially at air/water interface using THPC as a reducing agent as explained in chapter 4. This was followed by the introduction of 25 mL toluene containing 15 μmoles Ag(PPh₃)₄NO₃ solution over the rGO film and injection of Na₂S (7.5 μmoles) to the aqueous phase, heated to 90 °C for 1 hr. The as-synthesized hybrid films were collected on various substrates such as quartz, Si, and SiO₂ for further characterization. To study the effect of surfactant on Ag₂S nanoparticles preparation, we have used dodecyl amine (DDA) as a surfactant. 15 μmoles...
of DDA was added to toluene phase along with Ag precursor while performing the above reaction.

Figure 7.25. Schematic representation of rGO-Ag$_2$S nanocomposite films preparation by employing liquid/liquid interface a) One-step synthesis b) Two-step process.

7.9.3 Characterization

The X-ray diffraction patterns of the as-synthesized films were recorded using a Rigaku Smart Lab diffractometer equipped with parallel beam optics, and Cu-K$_\alpha$ radiation (40kV, 30mA) was incident at a grazing angle of 0.3°. UV-visible absorption spectra were recorded using a Lambda20 spectrometer. The films were collected on quartz for UV studies. Photoluminescence (PL) studies were carried out on a Flurolog-3 spectrophotometer. For PL studies, films were obtained on Si substrate. Field emission scanning electron microscopy (FESEM) images and energy dispersive X-ray spectroscopy (EDS) spectra have been achieved by a Nova NanoSEM600 (FEI, The Netherlands) instrument. For SEM imaging, the films were collected on Si substrates and washed and dried under an inert atmosphere. I-V characteristics of rGO based silver sulfide nanoparticle hybrids were measured by using a semiconductor characterization set-up, Keithley 4200 instrument. Films were collected on SiO$_2$ substrates with Ag paste contact pads for the study of electrical properties by the two-probe method.
7.10 Results and discussion

Ag$_2$S and rGO-Ag$_2$S NP films are prepared at the interface of toluene and water by in situ reaction and self-assembly in a single step and two step process. In this process, the Ag$^+$ ions in the organic phase can interact with the oxygen functional groups of GO in the aqueous phase or rGO film at the interface promoted by the increased thermal motion of the reactants during heating. During this process, Ag$^+$ ions also react with the S$^{2-}$ ions. The mechanism of one-step and two-step methods are described more detail in chapter 5.

To investigate crystal structure of as-prepared Ag$_2$S and rGO-Ag$_2$S NPs hybrid films, we have performed XRD diffraction. The XRD patterns of as-prepared hybrid films are shown in figure 7.26. Ag$_2$S film shows significant reflections at 28.9°, 31.5°, 33.6°, 34.4°, 34.7°, 36.8°, 37.7°, 40.7°, 43.5° and 44.3° corresponding to (111), (-112), (120), (-121), (022), (121), (-103), (031), (200), and (103) planes. All the peaks present in the XRD patterns are matched with the monoclinic Ag$_2$S (PCPDF File No. 14-0072) and small broadening of the peaks reveal the nanocrystalline nature of the particles. rGO-Ag$_2$S hybrid films prepared by two-step and single step methods have also shown similar peaks. The particle size of the Ag$_2$S NPs was calculated applying Debye-Scherrer formulae and given in the table 7.4.

![Figure 7.26. XRD patterns of as-synthesized hybrid films employing liquid/liquid interface (a) Ag$_2$S NPs (b) rGO-Ag$_2$S NPs hybrid film.](image-url)
\[ D = \frac{k \lambda}{\beta \cos \theta} \]  

where \( D \) is the crystallite size, \( k \) is a constant (shape factor for spherical particles) 0.91, \( \lambda \) is the wavelength of X-ray (Cu K\( \alpha = 1.5406 \) Å), \( \beta \) (in radians) is the full-width at half maximum of the most intense peak and \( \theta \) is the diffraction angle of the peak.

Table 7.4. Particles size of as-synthesized films of Ag\(_2\)S NPs and rGO-Ag\(_2\)S NPs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle Size (XRD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(_2)S NPs Film</td>
<td>16.70 nm</td>
</tr>
<tr>
<td>rGO-Ag(_2)S NPs hybrid film (single step)</td>
<td>10.57 nm</td>
</tr>
<tr>
<td>rGO-Ag(_2)S NPs hybrid film (two step)</td>
<td>14.36 nm</td>
</tr>
</tbody>
</table>

The surface morphology of the films studied by FESEM and the images are given in Figure 7.27. Figure 7.27a shows that Ag\(_2\)S films form a dendritic network like structure composed of nanoparticles and extends to a large area. The inset shows EDS spectra with peaks due to S and Ag species. Si signal is from the substrate. A higher atomic percentage of sulphur is observed indicating the presence of adsorbed sulphur ions on the Ag\(_2\)S films. Figures 7.27b,c show the morphology of rGO-Ag\(_2\)S hybrid films prepared employing liquid/liquid interface single-step and two-step methods, respectively. Ag\(_2\)S NPs observed on the surface of rGO layers in both the cases. The EDS spectral analysis in the inset shows the presence of C, S, and Ag species and Ag and S species are found in the atomic ratio 2:1. Ag\(_2\)S nanoparticles size may be tuned using different capping agents or surfactants. The optical properties and electrical properties of nanoparticles mainly depend on the size and different shapes. The size control of Ag\(_2\)S NPs has been reported using various capping agents such as oleylamine or dodecanethiol.(79) Here we have tried to control the size of the Ag\(_2\)S nanoparticles on the rGO surface using dodecyl
Figure 7.27. SEM images a) Ag$_2$S network like structure (b) rGO-Ag$_2$S nanocomposite prepared by liquid/liquid interface single step method (c) rGO-Ag$_2$S nanocomposite synthesized by liquid/liquid interface two-step method. The insets show EDS spectra.

Table 7.5. Elemental composition of as synthesised hybrid films from EDS analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C Wt%</th>
<th>C At%</th>
<th>S Wt%</th>
<th>S At%</th>
<th>Ag Wt%</th>
<th>Ag At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$_2$S NPs Film</td>
<td>-</td>
<td>-</td>
<td>20.1</td>
<td>45.85</td>
<td>79.9</td>
<td>54.15</td>
</tr>
<tr>
<td>rGO-Ag$_2$S NPs hybrid film (two-step)</td>
<td>11.17</td>
<td>47.09</td>
<td>10.11</td>
<td>15.97</td>
<td>78.71</td>
<td>36.94</td>
</tr>
<tr>
<td>rGO-Ag$_2$S NPs hybrid film (Single-step)</td>
<td>33.8</td>
<td>77.86</td>
<td>8.51</td>
<td>7.34</td>
<td>57.69</td>
<td>14.8</td>
</tr>
</tbody>
</table>

amine (DDA) as a surfactant. Figure 7.28 show FESEM image of the rGO-Ag$_2$S hybrid film prepared at liquid/liquid interface employing single step method with DDA as a surfactant. Ag$_2$S NPs covering the rGO surface are much smaller compared to that in figure 7.27 b and c though they have a very broad size distribution. The inset of fig.7.28a shows the EDS spectra with C, S, and Ag species.
Figure 7.28. (a) FESEM image of rGO-Ag$_2$S nanocomposite prepared in the presence of DDA surfactant by liquid/liquid interface single step method; Inset shows the EDS spectra (b) zoomed view of figure (a).

Figure 7.29. UV-Visible spectra (a) Ag$_2$S film (b) rGO-Ag$_2$S nanocomposite film prepared at liquid/liquid interface single step method (c) Two-step process.

Optical properties of as-prepared rGO-Ag$_2$S nanocomposites were studied using UV-visible and photoluminescence spectroscopy. Figure 7.29 shows the UV-visible absorption spectra of as prepared Ag$_2$S and rGO-Ag$_2$S nanocomposites. Ag$_2$S film (Fig. 7.29) shows a very broad absorption peak around 450 nm. This is similar to the absorption spectra observed for Ag$_2$S dendrites.(80) Hence, nanocrystalline Ag$_2$S absorb at a higher energy than bulk Ag$_2$S (Eg ~1 eV) due to quantum confinement. Figure 7.30 shows the photoluminescence (PL) spectra of as-prepared films. Fig.7.30a shows the PL spectrum of
Ag$_2$S film prepared by the single-step method and excited with $\lambda_{\text{ex}} = 325$ nm. The emission is seen at 400 nm along with shoulder peaks at 360 nm and 430 nm. The emission spectra of rGO-Ag$_2$S hybrid film prepared by two-step method with an excitation of 550 nm show a peak at 617 nm and shoulder bands at 590 and 630 nm (Fig. 7.30b). A weaker band at 700 nm is also observed. (80, 81) The PL bands can also be attributed to the contribution from Ag$_2$S nanocrystals on rGO and are in agreement with corresponding UV-visible spectra.

The defect states on Ag$_2$S surface, or a probable interaction with rGO may give rise to the shoulder bands. Xiang et al. have reported that Ag$_2$S nanospheres exhibit a broad absorption at 515 nm and emission at 630 nm. (81) Nanocrystals of Ag$_2$S with sizes less than 5 nm capped by ligands are reported to absorb in the range of 610-650 nm and emit in the range of 600-1200 nm. (82) Multiwalled carbon nanotubes coated with Ag$_2$S NPs have shown emission at 400 nm which is observed for Ag$_2$S network films in our case. (83)

Photocurrent response of Ag$_2$S and rGO-Ag$_2$S films were measured by performing I-V measurements in dark and light (incandescent lamp) conditions and are given in Fig. 7.31. A slightly nonlinear curve is seen for Ag$_2$S film (Fig. 7.31a) indicating semiconducting nature while the rGO-Ag$_2$S films (Fig. 7.31b) show linear variation with
higher current indicating an ohmic contact due to the presence of highly conducting rGO layers. The photoresponse during light irradiation showed enhancement in the electrical conductivity in the case of both films. Upon irradiation of light, both forward and reverse currents increased in both the samples. The photocurrents for Ag$_2$S and rGO-Ag$_2$S NPs are 30 nA and 265 µA while the dark currents are 16 nA and 190 µA at 10 V, respectively.

**Figure 7.31.** Photocurrent I-V measurements of the rGO-Ag$_2$S hybrid film (a) Ag$_2$S hybrid film in dark and light (b) rGO-Ag$_2$S hybrid film in dark and light.

### 7.11 Conclusions

We have explored the synthesis of hybrid systems of rGO based semiconductors including metal oxides and metal sulfides and studied the influence of doping with noble metal NPs to the metal oxide systems on their potential applications such as photodegradation and as reusable SERS substrates for fluorescent organic dye molecules.

We have synthesised ternary and binary systems of ZnO based rGO and rGO-Au hybrids with different morphologies such as nanoparticles and nanorods employing various chemical routes including solution-phase and hydrothermal methods. The morphological and crystalline studies by high-resolution electron microscopy reveal that they have excellent interfacial contacts between the components of hybrids. The synthetic routes influence the crystallinity, morphology, defect states and rGO content in the hybrids and influence the photocatalytic rates. Band-edge and visible emissions are
suppressed in the hybrids, accordingly higher photodegradation rates are provided by these combinations than bare ZnO NPs. rGO-Au-ZnO NPs has shown higher rate, 0.065 min\(^{-1}\), which is five times greater than bare ZnO NPs and 1.5 times greater than the rGO-ZnO NPs. rGO and Au components serve as mediums to the discharge of excited state electrons from ZnO conduction band, and the efficiency of hybrids is reduced when only one component is present. The effect of intensity of UV light on the degradation rates of the rGO-ZnO NRs catalyst is studied and expressed as a power law variation.

The enhanced photodegradation obtained by metal oxide nanostructures when combining with metal NPs or rGO is exploited to employ them as reusable or regenerate SERS substrates for the detection of fluorescent organic dyes. For this purpose, we have synthesized free-standing thin films of rGO based metal oxides and metal-metal oxide hybrid films employing liquid/liquid interface method by single step process. These are transferable to any desired substrates. The metal oxide NPs show the interesting morphologies including stacked hexagonal discs of ZnO, CuO splinters and SnO\(_2\) spheres embedded in rGO. Doping with Ag has modified disc-shaped ZnO to rice shaped nanoparticles. These hybrid films have been demonstrated as reusable SERS substrates for fluorescent dye molecules. The synergic effect provided by the dipole moment contribution of rGO and charge transfer between dye, rGO and metal oxides resulting in chemical enhancement and fluorescence quenching is exploited for SERS of adsorbed R6G dye. SERS and detection sensitivity of hybrid films are further improved by doping with Ag NPs in rGO-metal oxide systems due to surface plasmon mediated electromagnetic effect. The reusability of these hybrid films is demonstrated by SERS of another dye (MB) following photodegradation of R6G by metal oxides. A combined electromagnetic and chemical enhancement from metal, metal oxide and rGO can
contribute to SERS effect and metal oxides can degrade dye molecules when irradiated with UV light.

We have also demonstrated synthesis of ultra-thin films of Ag$_2$S and rGO-Ag$_2$S hybrids at a liquid/liquid interface employing in situ single step reaction approach for Ag$_2$S and single step as well as two step process for rGO-Ag$_2$S. These films can be transferred to any desired substrates for further studies or applications. Ag$_2$S films show dendritic structures that form a network and extend over a large scale area while rGO-Ag$_2$S films contain Ag$_2$S nanoparticles covering the rGO surface. In both cases, Ag$_2$S exhibit a monoclinic $\alpha$-Ag$_2$S structure. The as-synthesized hybrid films are conducting and show emission in the region 600-700 nm. The presence of a surfactant, dodecyl amine, in the reaction medium can aid in generating smaller particles. The photoresponsive studies of as-prepared hybrid films are conducted under the incandescent bulb and shows good photoresponsive behaviors.

7.12 References


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