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Materials Physics and Engineering Division

This division has been dedicated to develop state of the art materials, processes and technologies for Industrial and Strategic sectors through synergistic R&D efforts in the chosen areas. The division has active collaborations with different R&D organizations, such as, CSIR laboratories, DST, IITs, Delhi University (DU), etc. through developmental projects or higher educational programs.

The Soft and Polymeric Materials section is dedicated to research in fundamental and applied science of polymers, soft materials and liquid crystals. Research in liquid crystal has substantially grown in recent years. Ordering in these mesophases results in light transmission under crossed polarizers. NPL is focusing on the tuning of electro-optical properties of ferroelectric liquid crystals by doping with various types of nanomaterials like metal and metal oxide nanoparticles, quantum dots, carbon nanotubes and graphene etc. Recently the group has started diversification in the field of liquid crystals into non-display applications also, such as development of biosensors based on liquid crystals, studying the dynamics of liquid crystal interface with various immiscible fluids etc. Also, the group has been developing high performance microwave absorption material for the radar absorbing application through encapsulation of barium strontium titanate (BST) and expanded graphite (EG) in polyaniline (PANI). A tubular core-shell morphology having reduced graphene oxide (rGO)/γ-Fe$_2$O$_3$ in polyaniline (PANI) core is developed as high shielding effectiveness/EMI absorbable material. The fabrication of SWNTs/graphite nanoplates(GNPs) hybrids based field-effect transistor (FET) devices demonstrated for the label free detection of cardiac biomarkers for the diagnosis of cardiovascular diseases (CVD).

The Physics and Engineering of Carbon section has synthesized low cost high yield continuous carbon nanofibers from PAN and PVA polymers using a novel “Electrospinning” technique. Lightweight carbon foams (CFoams) decorated by Fe$_3$O$_4$ and ZnO nanoparticles are developed that have demonstrated excellent EMI shielding response. Under a CSIR-TAPSUN project (NWP-56), nanosized SnO$_2$ incorporated long length MWCNTs are used to develop free standing binder less conducting paper, which is successfully demonstrated as anode in lithium (Li)-ion battery at CECRI-Karaikudi, MWCNTs supported platinum is also synthesized as catalyst for the development of cost competitive PEM fuel cell.

The Luminescent Materials and Devices section has fabricated a dual excitation, dual emission phosphor by simultaneously doping of lanthanide ions Er$^{3+}$, Yb$^{3+}$, Eu$^{3+}$ in a highly efficient host YVO$_4$ for solar cell application. It is demonstrated that silver nanopism (Ag NP) generates near field and act as multipolar nano-antenna. A novel red-emitting Gd$_3$(CaZnO)$_4$:Eu$^{3+}$ (GCZO:Eu$^{3+}$) nanophosphor system is developed. Further efforts are underway to develop Gd$_3$(MoO$_4$)$_3$:RE (Eu, Er, Yb) nanophosphor as a Broad Spectral converter (UV-IR) for promising Next Generation silicon solar cells.

The Multiferroics and Magnetics section has developed capability for the precise calibration of NMR Teslameeter and successfully installed Cesium Magnetometer as a primary standard. Onsite survey for electromagnetic radiation and calibration of ELF/EMF meters is initiated. Thin films of Magnesium ferrite, ceria added magnesium ferrite and BaTiO$_3$ doped with 0.1 at% Cr (Cr:BT0) are developed by the pulsed laser deposition technique. Spin pumping induced spin-Hall effect is investigated in RF sputtered Co/Pt bilayer thin film spintronics application.

The Biomedical Instrumentation section has successfully established a DST center for biomolecular electronics. Two prototype devices for the detection of total cholesterol are developed. Stable cationic poly (lactic-co-glycolic acid) (PLGA) microspheres encapsulating the iron oxide nanoparticles are synthesized for the development of a DNA biosensor. Controlled synthesis of electroactive gold nanoparticles (AuNP) is conducted and biosensing performance is investigated. A label-free CysCdS-Au biosensor platform/device is developed to investigate the biomolecular interactions.

The Metals & Alloys Group has synthesized Cu$_2$SbSe$_3$ thermoelectric material with intrinsically ultralow lattice thermal conductivity for the development of thermoelectric devices. A new half-Heusler Derivative Zr$_2$Ni$_2$Sn$_2$ Bulk Nanocomposite with enhanced thermoelectric performance is developed. The development of novel Rare-Earth Free Permanent Magnetic Materials, e.g., MnAl, Mn-Bi-Fe, manganese antimonide, etc is under progress using the melt spinning technique. Lightweight and high strength Aluminum-carbon nanotube composites are also under development using cryomilling and hot extrusion.
Polymer and Soft Materials

Faster display devices with improved contrast based on MgO nanoparticles/ferroelectric liquid crystal composites

We have studied and reported that by dispersing magnesium oxide nanoparticles (MgO NPs) into the host ferroelectric liquid crystal (FLC) W301, MgO NPs/FLC composite showed significantly faster response and improved optical tilt angle. The fastening of response time in MgO NPs/FLC composite has been attributed to the decrease in rotational viscosity and increase in surface anchoring energy. Due to the enhanced surface interaction of MgO NPs having surface defects with mesogens, a strong surface anchoring is experienced on the FLC molecules that not only fastened the response but also improved the optical tilt angle of the MgO NPs/FLC composites, which ultimately resulted in improved contrast. A systematic approach has been followed to elucidate an idea of designing faster display devices with improved contrast based on MgO NPs/FLC composites. Nanosized particles of MgO were synthesized via hydrothermal method from magnesium nitrate (MgNO₃·6H₂O), sodium hydroxide (NaOH) and de-ionized water (H₂O) as precursors in appropriate amount. From electron microscopic investigation, it has been seen that the size of these NPs ranged between 30 to 60 nm with an average size of about 50 nm. The MgO NPs/FLC composite was prepared by adding various concentrations (wt.%) of nanopowder of MgO NPs with the FLC material. The mixture was then ultrasonicated for about 40 min. in the isotropic phase of the FLC material to ensure the homogeneous dispersion of MgO NPs in the FLC host material. The pure and MgO NPs doped W301 material were then introduced into the LC sample cells by means of capillary action at temperature just above the isotropic transition temperature.

Faster electro-optic response of MgO NPs/FLC composites

The electro-optic response time at room temperature (25 °C) for various concentrations of

![Fig 2.1: Behaviour of (a) response time (τ), (b) rotational viscosity (γ), (c) spontaneous polarization (Ps), and (d) optical tilt angle (θ) of pure and different concentrations of MgO NPs doped FLC material W301 at room temperature](image)
MgO NPs doped FLC material, W301 as a function of applied voltage and a comparison with pure W301 is shown in Fig. 2.1(a). It is clearly seen from the Fig. 2.1(a) that the MgO NPs/FLC composites respond faster than pure W301 and the response time shows a strong dependence on MgO NPs concentration. On the systematic assessment of the response time of composites with different concentration of MgO NPs, 0.5 wt.% showed the fastest response and it had fastened the response time by ~50% than the pure FLC. From Fig. 2.1(a), it is seen that the value of response time of pure W301 is 1.6 ms at an applied voltage of 4 V whereas, 0.5 wt.% MgO NPs doped W301 showed its electro-optic response in 0.8 ms.

The rotational viscosity of LC material is directly related to its response time as follows;

\[ \tau = \frac{\gamma}{P_s E} \] ...........................(1)

where \( \tau \) is response time, \( \gamma \) is the rotational viscosity, \( P_s \) is the spontaneous polarization, and \( E \) is the applied electric field respectively. It is seen from Fig. 2.1(b) that the rotational viscosity of the FLC material W301 is decreased on doping with MgO NPs, which is in good agreement with the above mentioned relation. The reduction in rotational viscosity is attributed mainly due to two reasons. Firstly, due to the non-trivial dielectric anisotropic properties of the MgO NPs and FLC material, both experience a torque on the application of electric field and hence rotational viscosity is decreased. Secondly, perturbations in order parameters such as spontaneous polarization and optical tilt angle of FLC material on doping with MgO NPs reduce the rotational viscosity of FLC, which is illustrated in Fig. 2.1(c) and Fig. 2.1(d).

Surface anchoring energy and cell gap of LC also play a key role in LC response time. The relation between response time and anchoring energy for strong anchoring is as follows;

\[ \tau = K_{33} \left( \gamma^* + \frac{K_{33}}{E} \right) \] ...........................(2)

where \( \tau \) is the response time, \( \gamma \) is the rotational viscosity, \( K_{33} \) is the bent elastic constant, \( d \) is the cell gap and \( W \) is the anchoring energy strength coefficient respectively. It is clear from the above mentioned equation that response time is reduced on increase of anchoring energy strength.

Enhancement in optical tilt angle and contrast of MgO NPs/ FLC composites

As seen in Fig. 2.1(d), the optical tilt angle is enhanced on doping with MgO NPs and it is having a strong dependence on MgO NPs concentrations. Here, on doping with 0.5wt% of MgO NPs the value of tilt angle showed an increment of ~2.5\(^\circ\) in all applied voltages above 1 V. The MgO NPs used in this study is having a non-zero dipole moment along (111) plane (ref.: JCPDS file no. 870652, lattice parameter: \( a = 0.4211 \) nm). Thus the MgO NPs having inherent dipole moment interact with the dipolar mesogens, which results in the improvement of optical tilt angle. Improvement in optical tilt ultimately leads to the improvement of contrast of LC displays.

Fig. 2.2 exhibits a schematic diagram of the interaction of MgO NPs with mesogen. Due to the dipole-dipole interaction between the FLC molecules and NPs a strong intrinsic field inside the sample is created.

Fig. 2.2: Schematic representation of MgO NPs doped W301 material filled cell

The optical micrographs indicating the dark and bright states of pure (Fig. 2.3(a) and (b)) and doped samples (Fig. 2.3(c) and (d)) are shown. From this figure it is seen that the molecular alignment of FLC material, W301 is improved on doping with MgO NPs. The light leakage in the dark state of doped samples (Fig. 2.3(c)) is also reduced, giving an improved darkness due to the dipole-dipole
interaction and increase of surface anchoring strength of FLC with NPs. The bright state (Fig. 2.3 (d)) also shows an improved texture than pure W301 (Fig. 2.3(b)).

For quantifying this, we had taken the characteristics of optical spectrum intensity with wavelength of pure and doped samples. Fig. 2.4 shows the fitted data of the optical spectrum intensity versus wavelength from spectrum analyzer of the pure and doped samples at dark state (Fig. 2.4(a)) and bright state (Fig. 2.4(b)).
It is clearly seen from the Fig. 2.4(a) that the intensity of dark state is less for the doped sample while the intensity of bright state is almost doubled (Fig. 2.4(b)) than the pure W301. A clear confirmation of improvement of contrast is obtained from this, where the dark state of the sample became darker and the bright state became brighter on doping with MgO NPs.

This report systematically presented the feasibility of fabricating MgO NPs/FLC composites having faster response time with improved contrast for future display applications and other electro-optic applications, such as beam steering or polarization shutters.

**Self assembled monolayer based liquid crystal biosensor for free cholesterol detection**

A unique cholesterol oxidase (ChOx) liquid crystal (LC) biosensor, based on the disruption of orientation in LCs, is developed for cholesterol detection. A self-assembled monolayer (SAM) of Dimethylolctadecyl [3-(trimethoxysilyl)propyl] ammonium chloride (DMOAP) and (3-Aminopropyl) trimethoxy-silane (APTMS) is prepared on a glass plate by adsorption. The enzyme (ChOx) is immobilized on SAM surface for 12 h before utilizing the film for biosensing purpose. LC based biosensing study is conducted on SAM/ChOx/LC (5CB) cells for cholesterol concentrations ranging from 10 mg/dl to 250 mg/dl. The sensing mechanism has been verified through polarizing optical microscopy, scanning electron microscopy, and spectrometric techniques.

The schematic of whole procedure is shown in Fig. 2.5, which highlights the design of the current LC based biosensor. It is well known that alignment of LC is highly dependent on the surface effects. A slight change on the surface leads to change in the alignment of LC molecules, which can be detected through a polarizing optical microscope (POM). This notion is used in the present study. For this purpose, a reference cell is used to achieve the homeotropic alignment of 5CB using above mentioned SAM. In this configuration, no light is passed through the LC cell. The presence of cholesterol can be detected in terms of non-zero transmitted light intensity through the LC cell containing cholesterol solution.

![Schematic showing idea and working of proposed liquid crystal based cholesterol biosensor.](image1)

**Fig. 2.5:** Schematic showing idea and working of proposed liquid crystal based cholesterol biosensor: (a) No light transmission in case of homeotropic alignment (b) Slight transmission of light due to the presence of ChOx (c) Maximum light transmission in case of homogeneous alignment caused due to the presence of cholesterol.

![Intensity of transmitted light through liquid crystal cells as a function of wavelength recorded using a spectrometer for...](image2)

**Fig. 2.6:** Intensity of transmitted light through liquid crystal cells as a function of wavelength recorded using a spectrometer for (a) reference cell (b) enzyme cell (c) biosensing cell with cholesterol concentration as 10 mg/dl (d) 50 mg/dl (e) 150 mg/dl and (f) 250 mg/dl.

Here, the intensity of transmitted light through different surface treated LC cells is measured with a spectrometer and plotted as a function of wavelength. The various plots are shown in Fig. 2.6. It can be inferred that the intensity increases with an increase in cholesterol concentration. The homeotropic alignment resulting from the reference cell shows the lowest intensity, which acts as a reference and shown as 1. However, immobilization of ChOx enzyme itself...
brings change in the alignment and thus shows higher intensity relative to reference, which is shown as 2. The various cholesterol concentrations show regular increment in intensity (3, 4, 5 and 6), which is the basis of cholesterol sensing. The intensity versus concentration of cholesterol is plotted and shown as inset of Fig. 2.6. Figure 2.6 simply summarizes the understanding and the working idea of LC based cholesterol biosensor.

**Tailored polyaniline/barium strontium titanate/expanded graphite multiphase composite for efficient microwave absorption**

Designing of high performance microwave absorbing material using a simple, cost-effective and scalable method by encapsulating barium strontium titanate (BST) and expanded graphite (EG) in polyaniline (PANI) matrix in the presence of dodecybenzene sulfonic acid (dopant) in aqueous medium by chemical oxidative polymerization is reported. Different formulations have been prepared to study the effect of dielectric constituent on the electrical and dielectric properties of polyaniline composite. The optimum dielectric properties due to incorporation of BST and moderate conductivity due to embedded EG in PANI matrix collectively contribute in designing an absorption based shield. One of the formulation shows shielding effectiveness due to absorption more than 50 dB (>99.999 % attenuation) while reflection loss less than 1 dB in Ku-band (12.4-18 GHz) frequency range. Since, observed attenuation of this absorption dominated shielding is greater than the recommended limit (30 to 40 dB) of commercial application therefore these are potentially applicable as radar absorbing material. The morphologies of BST, EG, PANI and PANI composites were investigated using SEM Fig. 2.7 (a) illustrate the BST nanoparticles derived from citric precursor method. In general, chemically derived BST nanoparticles results agglomeration similar to previous observations.

![SEM image](image)

Fig. 2.7: SEM image (a) BST (b) EG (c) DBSA doped PANI and (d) PANI Composite
The EG consisted folded and wrinkled sheets that were randomly aggregated and their sizes are up to a few micrometers as seen in Fig. 2.7 (b). Fig. 2.7 (c) shows the SEM image of DBSA doped PANI. The resulting PANI powder was homogeneous and form agglomerates with different sizes rock shapes. SEM micrograph of PBE121 composites revealed the presence of BST particles and EG sheets. BST particles are appearing as bright dots due to their nanostructure and EG appear as sheets (Fig. 2.7d).

Fig. 2.8 (a) shows the total SE while Fig. 2.8 (b) illustrates the SE$_a$ and SE$_r$ of PANI and its composites. The SE value of 26, 71, 81, and 54 dB is achieved for PANI, PBE111, PBE112 and PBE121, respectively. Composite PBE121 gives very interesting SE result with SE$_a$ more than 50 dB and SE$_r$ less than 1 dB in entire frequency range. From the detailed shielding analysis, it has been observed that at 15.0 GHz, SE$_a$ value increases with increase in EG content while SE$_r$ have no significant change. Moreover SE$_a$ and SE$_r$ decreases with increasing content of BST in PANI-EG matrix. When the BST content reaches 9 wt% in PANI-EG matrix the SE$_r$ values obtained less than 1 dB which is minimum value of reflection achieved so far with retaining optimum microwave absorption. EMI shielding using highly conducting materials such as metals is governed by reflection rather than absorption. On the other hand, hybrid conducting composite provide EMI shielding predominantly due to absorption, owing to the presence of electric dipoles.

**Encapsulation of γ-Fe$_2$O$_3$ decorated reduced graphene oxide in polyaniline core-shell tubes as an exceptional tracker for electromagnetic environmental pollution**

The ultimate goal of development of a new material γ-Fe$_2$O$_3$ decorated reduced graphene oxide (rGO):Polyaniline (PANI) core-shell tubes has been done for absorbing electromagnetic interference (EMI) pollution. Herein, we report the synthesis and characterization of a PANI tubes consisting of rGO decorated with iron oxide nanoparticles (RF). The intercalated RF was synthesized by thermal decomposition of ferric acetyl acetonate in reducing atmosphere. Furthermore, RF was further encapsulated through the oxidative polymerization of aniline in the presence of β-Naphthalene sulphonic acid which results in RF/PANI core-shell morphology. Scanning electron microscopy results confirm the formation of tubular core-shell morphology having 5-15 µm length and 1-5 µm diameter (Fig. 2.9). The presence of rGO/ γ-Fe$_2$O$_3$ in PANI core enhances the interfacial polarization and the effective anisotropy energy of the composite which contributes to more scattering and leads to the high shielding effectiveness.
Fig. 2.9: SEM images of (a) iron oxide nanoparticles derived from Fe(acac)₃ by thermal decomposition at 186°C, (b) reduced graphene oxide sheets decorated with \( \tilde{\alpha} \)-Fe₂O₃ nanoparticles, (c) PRF10 and (d) PRF13, showing the formation of tube like structure with RF particles inside the tubes.

\( \text{SE}_1 \approx 51\text{dB} \) at a critical thickness of 2.5 mm. Additionally, the effective complex permeability and permittivity parameters of composites have been evaluated from experimental scattering parameters (S11 & S21) using theoretical calculations given in Nicholson*Ross and Weir algorithms.

**Synthesis of ferrofluid based nanoarchitectured polypyrrole composites and its application for electromagnetic shielding**

The monodispersion of magnetic nanoparticles in conducting polymer is the
Materials Physics and Engineering

prerequisite to make a high quality composite for tunable electromagnetic interference (EMI) shielding. To meet this challenge, we have designed and synthesized ferrofluid based nanoarchitectured polypyrrole composites containing Fe₃O₄ (8-12 nm) via in situ oxidative polymerization as shown in Fig. 2.10. To tune the microwave signals, polypyrrole composites (PFF) with different monomer/ferrofluid weight ratios have been prepared and characterized in microwave frequency domain. A maximum shielding effectiveness value of $SE_{\text{max}}$ (~ 20.4 dB (~99% attenuation) due to the absorption of microwave has been observed in the frequency range of 12.4-18 GHz and attenuation level varied with ferrofluid loading. The electrical conductivity of PFF composite is of the order of $10^2$ S cm⁻¹ order and having superparamagnetic nature with saturation magnetization (Ms) of 5.5 emu g⁻¹. The lightweight PFF composites with high attenuations can provide full control over the atomic structure and are favorable for the practical EMI shielding application for commercial electronic appliances.

The variation of the SEA and SER with frequency for PPy and PFF composites in 12.4-18.0 GHz (Ku-band) is shown in Fig. 2.11. From the figure, it has been revealed that PFF composites show absorption dominated SE rather than reflection. In polypyrrole composite sheets with matching thickness of ~ 2.0 mm, maximum SE due to absorption (SE_{ absorp}) has been ca. 20.4, 18.6 and 18.1 dB for PFF13, PFF12, and PFF11 samples at 18.0 GHz, respectively whereas the SEA(max) value of 17.6 dB has been observed for Py. For the reflection part, $SE_{ref}$ has been ca. 3.1, 2.9, 2.5 and 5.2 dB for PFF13, PFF12, PFF11 and PPy samples at 18.0 GHz, respectively. The results demonstrate that the absorption of microwave and overall shielding effectiveness ($SE = SE_{abs} + SE_{ref}$) up to 23.5 dB (~ 99.5% attenuation) for PFF13, increases with the concentration of the ferrofluid in the composite. The increase in the absorption with the addition of ferrofluid in PFF samples may be attributed to the higher dielectric and magnetic losses induced by Fe₃O₄ nanoparticles present in ferrofluid. In case of PPy, absorption is still the dominating factor but the reflection part is on the higher side, which makes it less favorable as microwave absorbing material.

**Designing of green chitosan-polymer composite coatings for corrosion protection of mild steel in saline conditions**

Chitosan-polypyrrole-SiO₂ composites were synthesized by chemical oxidative polymerization of pyrrole in chitosan solution using FeCl₃ as an oxidant. The synthesized composites were loaded...
Table 2.1: Different electrochemical parameters obtained by Tafel extrapolation in 3.5% NaCl solution

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Loading of composite</th>
<th>Ecorr (mV)</th>
<th>Icorr (nA/cm²)</th>
<th>Rp (KΩ)</th>
<th>Protection Efficiency (% P.E.)</th>
</tr>
</thead>
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<td>8.45x102</td>
<td>31.87</td>
<td>-</td>
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<tr>
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<td>3.27</td>
<td>20580</td>
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</table>

in epoxy resin and subsequently coated on mild steel substrates using powder coating technique. XRD and FTIR analyses show a synergistic interaction between chitosan and polypyrrole. Microstructural analyses reveal the formation of polymer particles with distinct spherical morphology. SiO₂ particles embedded in the polymer matrix are clearly noticed from the FE-SEM micrographs. TGA thermograms show a better thermal stability of chitosan-polypyrrole-SiO₂ composite as compared to polypyrrole-SiO₂ composite (without chitosan). DSC curves reveal a high cross linking density for epoxy coatings loaded with chitosan composite. Tafel plots exhibits a significantly low value of corrosion current density (icorr) for epoxy coatings with 2 wt% loading of chitosan-polypyrrole composite.

The corrosion protection efficiency (% P.E.) is measured to be maximum (99.97 %) for the epoxy coatings with 2 wt% loading of chitosan-polymer composite as given in Table 2.1. The weight loss measurements and salt spray test results clearly exhibit a significantly high corrosion resistance of chitosan-polymer composite coated mild steel substrates. Photographs of epoxy coated mild steel samples and polymer incorporated into epoxy powder coated on mild steel panels after 65 days under salt spray conditions is shown in Fig. 2.12.

**Label free detection of cardiac biomarkers for the diagnosis of cardiovascular diseases**

Cardiovascular disease (CVD) is the leading cause of morbidity and mortality worldwide and accounts for approximately half of all the deaths within the western world. Coronary ischemia is the root cause of acute myocardial infarction (AMI). As MI causes irreversible damage to the heart, a

Fig 2.12: Photographs of (a) epoxy coated and epoxy with (b) 1.0 wt%, (c) 2.0 wt% loading of chitosan-polypyrrole-SiO₂ composite (CsPC) coated mild steel specimens exposed to salt spray fog after 65 days
patient suspected of MI must be diagnosed quickly, efficiently, and comprehensively based on the information obtained from the measurement of cardiac specific biomarkers within the patient’s blood. Hence, cardiac markers continue to play a major role in the diagnosis and management of patients suspected of having myocardial damage or AMI. Previously, the commonly used biomarkers for early detection of CVD included the MB isoenzyme of creatine kinase (CK-MB) and myoglobin. However, in the recent years, CK-MB has been replaced by cardiac troponin I (cTnI), a more specific biomarker. Based on literature data and clinical assessments, cTnI levels greater than 1.2 ng mL⁻¹ is taken as the definition of AMI, making a cut off value of 0.1 ng/ml of cTnI to identify patients at higher risk for very early adverse outcomes.

We demonstrate the fabrication of single walled carbon nanotubes (SWNTs)/graphite nanoplates (GNPs) hybrids based nanoelectronic chemiresistive/FET device for the quantitative detection of cTnI (schematic shown in Fig. 2.13). The GNPs capped with 3-mercaptopropionic acid (MPA) are attached to SWNT through an organic molecular bilinker 1-pyrenemethylamine. The highly specific cTnI antibody was covalently immobilized on GNPs through capping agent using carbodiimide coupling reaction. The cTnI interaction to its corresponding complementary antibody was studied with respect to changes in conductance in SWNTs channel, and a detailed field-effect transistor characteristic (FET) was delineated.

The fabrication of the device at each step of surface modification of the aligned SWNTs was monitored by recording the current-voltage (I-V) characteristics from -0.5V to +0.5V (Fig. 2.14a). Fig. 2.14b shows the dependence of the source-drain current, Iₓ, on the back gate voltage, Vₓ, of the SWNTs FET after each surface modification steps in the range -40 to +40 V, at a drain voltage (Vₜ) of 0.1V.

It has been found that the charge transfer characteristic in SWNT hybrid device upon biomolecular functionalization is governed by the electrostatic gating effect without showing much change in the charge mobility. To investigate the sensitivity of the hybrid device, it was exposed to varying concentrations of target antigen cTnI in PBS (pH 7.4). Fig. 2.15 shows the normalized response of the cTnI-GNP/SWNTs hybrid [(Rₓ-Rₒ)/Rₒ, where Rₒ and R is the resistance of the device measured before and after exposure to cTnI, as a function of cTnI concentration in PBS. The device exhibited a
linear response to cTnI from 0.01 to 10 ng mL\(^{-1}\) with a sensitivity of about 20% per decade ng mL\(^{-1}\) cTnI. The stepwise construction of the prototype assembly is represented in Fig. 2.16.

Fig. 2.15: Calibration curve of cTnI and mouse IgG detection on cTnI-GNP/SWNTs chemiresistive biosensor

Fig. 2.16: Schematic representation of the stepwise fabrication of the bioelectrode

We also demonstrate a facile strategy to synthesize a ZnS-RGO nanocomposite consisting of 3-mercaptopyrrole acid (MPA) capped ZnS nanocrystals, ZnS(MPA), anchored on RGO sheets through a linker and deposited onto silane modified indium-tin-oxide (ITO) glass plate for the fabrication of a bioelectrode. In this work, we have utilized large surface ZnS (MPA) nanocrystals, where the surrounding carboxyl functional groups provided a high loading of protein antibody, Ab-cMb, molecules through strong carbodiimid linkage. The stepwise fabrication of the GO nanosheets, spectroscopy (EDXS attached with TEM) was performed (Fig. 2.17). Fig. 2.17a is a bright field micrograph of a nanocomposite of GO with ZnS. The EDXS spectrum exhibits the presence of the peaks corresponding to energy levels of C (0.277 keV; Ka), Zn (1.011 keV; La and 8.631 keV; Ka), S (2.30 keV; Ka) and Cu (0.929 keV; La and 8.0431 keV; Ka),
as displayed in Fig. 2.17b. The elemental distribution of C, Zn and S is shown in Fig. 2.17c, d and e, respectively. The overlapped elemental mapping of all three elements (C, Zn, S) is shown in Fig. 2.17f, suggesting a uniform distribution of ZnS NPs throughout the GO nanosheets.

A detailed electrochemical immunosensing study has been carried out on the bioelectrode towards the detection of target cardiac specific biomarker antigen myoglobin, Ag-cMb. The optimal fitted equivalent circuit model that matches the impedance response has been studied to delineate the biocompatibility, sensitivity and selectivity of the bioelectrode. The bioelectrode exhibited a linear electrochemical impedance response to Ag-cMb in a range of 10 ng to 1 μg mL$^{-1}$ in PBS with a sensitivity of 177.56 &l;I cm$^{2}$ per decade. The impedimetric sensing performance of the bioelectrode with ZnS-RGO nanocomposite towards the quantitative detection of target protein antigen, Ag-cMb, in PBS was studied and compared with that of native RGO sheets without ZnS nanoparticles, to highlight the contribution of the ZnS nanoparticles in the overall enhanced immunosensing performance.

### Physics and Engineering of Carbon

#### Development of continuous Carbon nanofibers by Electrospun

In this project the continuous carbon nanofibers are synthesized by electrospinning technique from PAN and PVA polymer. The carbon nanofibers synthesis from the PVA is a challenging task because it gets degraded during heat treatment. Therefore in the present project, the high yield carbon nanofibers are developed from polyvinyl alcohol by applying a special technique. Fig. 2.18 shows the SEM image of PVA nanofibers (2.18a) and carbon nanofibers (2.18b). The diameter of electrospun PVA nanofiber is in the range of 300-350 nm while that of carbon nanofibers is 200-250 nm. These low cost carbon nanofiber can be used for low cost filtration, super capacitor, anode materials for batteries and medical applications.
Carbon foam decorated with magnetic and dielectric nanoparticles to improve microwave absorption

Carbon foams (CFoams) are sponge-like high performance light weight engineering materials possess excellent electrical and mechanical properties as well as thermal stability. In CFoam, pore walls i.e., ligaments, are interconnected to each other, that are responsible for the conduction path and hence contribute to high electrical conductivity due to mobile charge carrier (delocalized π electron). The high value of electrical conductivity causes the CFoam as an electromagnetic radiation reflector rather than absorber. While in certain application shielding materials have mandatory to absorb maximum electromagnetic radiation. Therefore, to improve the absorptivity of electromagnetic radiation in light weight CFoam, the CFoams are decorated by Fe₃O₄ and ZnO nanoparticles (Fig. 2.19a). Inset of the figure shows the Fe₃O₄ nanoparticles and evolution of ZnO nanorods. It is observed that Fe₃O₄ and ZnO nanoparticles coating not only improved the absorption losses but also enhanced the compressive strength of CFoam by 100%. The CFoam demonstrate excellent shielding response in the frequency range 8.2 to 12.4 GHz in which total shielding effectiveness (SE) dominated by absorption losses. The total shielding effectiveness is -48.5 dB and it is governed by absorption losses -41.5 dB (Fig. 2.19b).

Synthesis and development of graphene based polymer composite: Its application in polymer electrolyte membrane fuel cells (DST project)

In this project, we are synthesizing high quality graphene by chemical vapor deposition (CVD) technique by indigenously fabricated CVD setup in the Laboratory. The single layer graphene
(SLG) synthesized on the high purity copper substrate and transferred on the Silicon substrate. Fig. 2.20a shows the SEM micrograph of graphene sheet on the copper substrate. The graphene is transferred from copper substrate to SiO₂/Si by etching copper by chemical method. Fig. 2.20b shows the graphene sheet in which some portion is folded. Fig. 2.20c shows Raman spectra of single layer graphene in which intensity ratio of 2D/G is more than three.

Development of carbon based anode for Li-ion Battery (under CSIR-TAPSUN project NWP-56)

a) Under the CSIR-TAPSUN project, using a novel technique nanosize SnO₂ incorporated in house grown long length multiwalled carbon nanotubes are used to make free standing binder less conducting paper of size 20 cm × 20 cm (Fig. 2.21a). The SnO₂ particles were uniformly attached on the surface of MWCNTs as shown in the FESEM image (Fig. 2.21b). These electrodes showed a discharge capacity of 496 mAh/g for more than 100 cycles at C/5 rate (Fig. 2.21c). This anode was used in a Li-ion battery at CECRI, Karaikudi to successfully demonstrate for lighting a solar lantern up to 6 h (Fig. 2.21d). A patent has already been filed on this process and few industries are interested in this product.

b) Mesocarbon microbeads (MCMB) were prepared from heat treatment of coal tar pitch and petroleum pitch under reduced pressure in a

Fig. 2.21: (a) Optical image of free standing SnO₂/MWCNT composite anode of size 20cm × 20cm, (b) FESEM image of SnO₂/MWCNT composite (c) discharge capacity of MWCNT and SnO₂/MWCNT composite anode and (d) demonstration of lighting of solar lantern using SnO₂/MWCNTs anode based Li-ion battery
distillation assembly. These pitches were again heated in furnace at 390 °C in an inert atmosphere. In optical texture, small mesophase spherules of size varying from 45 to 65 μm embedded in pitch were clearly seen (Fig. 2.22a). These spherules were then extracted with tar oil and quinoline to separate MCMB from pitch. Scanning electron micrograph of extracted MCMB is shown in Fig. 2.22b. Microstructure of the MCMB looks spherical bead like structure with average particle size of 50 μm.

Further modifications of MCMB with some metal oxides are continued and then the samples will be sent to CSIR-CECRI, Karaikudi for electrochemical study for electrochemical characterization (charging/discharging capacity) and suitability for anode of Li ion battery.

**Development of Carbon Nanotube supported Platinum as Catalyst for PEM Fuel Cell**

Conventionally carbon black supported Platinum is being used as Fuel cell catalyst that gives a PEM fuel cell power density of nearly 700 – 800 mW/cm² with a platinum loading of 0.5 mg/cm² on both the electrodes (Fig. 2.23a). Studies have been carried out whereby multiwalled Carbon Nanotube (MWCNTs) supported Platinum has been developed as Catalyst for PEM Fuel Cell. The high surface area of MWCNTs can lead to better utilization of the available catalyst. Hence similar PEMFC performance has been achieved with 0.25 mW/cm² of Pt loading as shown in Fig. 2.23b. Thus by reducing the amount of Platinum to 50 % the technology can go a long way in developing cost competitive fuel cells.
Development of advanced carbon materials and products for very high power MW Tubes

The high density graphite samples were prepared by using semi-coke (SC) powder obtained from heat treatment of coal tar pitch by mixing with additives such as natural graphite (NG), synthetic graphite (SG) and carbon black (CB) through ball milling. The mixed powders of different carbonaceous materials were moulded into blocks using cold isostatic press and carbonized to 1000°C and higher up to 2200°C in an inert atmosphere to obtain high density graphite sample. Iso-moulds of high density graphite of size dia. 30 mm and height 70 mm were machinable and possess density of 1.76 g/cm³, bending strength 68 MPa and electrical resistivity 2.0 mΩcm.

Samples of copper reinforced graphite were prepared by mixing different carbonaceous powders such as coal tar pitch (CTP), SC, NG, SG, CNT with copper (Cu) using powder metallurgy method. The mixed powders were moulded into blocks using hydraulic press of size dia. 55 mm and height 23 mm and then carbonized upto 1000 °C in an inert atmosphere. The properties were measured after heat treatment to 1000 °C and found to be density of 2.49 g/cm³, bending strength of 49 MPa and electrical resistivity of 1.7 mΩcm.

Luminescent Materials and Devices Group

Fabrication of dual excitation dual emission phosphor with plasmonic enhancement of fluorescence for simultaneous conversion of solar UV and IR to visible radiation

A dual excitation, dual emission phosphor has been fabricated by simultaneous doping of lanthanide ions Er³⁺, Yb³⁺, Eu³⁺ in a highly efficient host YVO₄ which is simultaneously excitable by UV and IR radiation and dual emission i.e., fluorescence in bright red under UV excitation and intense green under IR excitation (Fig. 2.24). A direct assembly of Ag nanoparticles (NPs) and YVO₄; Er³⁺, Yb³⁺, Eu³⁺ on a suitable substrate showed enhancement of fluorescence of Eu³⁺ red emission under UV excitation. Such studies indicate that two dimensional conformal transparent layer of Ag NP-phosphor combine on a silicon solar cell may be used as DC and UC solar spectrum converter from UV/IR to visible region where spectral response of Si is high.

Fig 2.24: Dual excitation phosphor with simultaneous conversion capability of solar UV and IR radiation to red and green light
Silver Nanoprism Acting as Multipolar Nano Antennas under Low Intensity Infrared Optical Field Excites Fluorescence from Eu³⁺

Silver nanoprisms (Ag NP) generates near field due to multipolar surface plasmon resonance (SPR) and lightening nod effect and act as multipolar nano antenna. The ability of Ag NPs to create such effect even under infra red (IR) optical field far off resonance from the SPR frequency is demonstrated through Finite difference time domain simulations of exact Ag NP and hybrids. The conclusive experimental proof of such near field around Ag NPs under low intensity (2mW) IR (980nm) light came when it could excite fluorescence from YVO₄:Eu³⁺ nanoparticles which otherwise do not fluoresce under IR. The results (Fig. 2.25) open up new vistas for exclusive plasmonic excitation of fluorescence through metal NP hybrids/ensembles.

Silver nanopism enhanced fluorescence in YVO₄:Eu³⁺ nanoparticles

Silver nanoproms of different sizes influence fluorescence enhancement in YVO₄:Eu³⁺ nanoparticles to various degrees under excitation of green light (532 nm). Local field generated by silver nanopism and their dimers is simulated through FDTD method and a direct correlation with fluorescence enhancement is established.

Hot electron injection in carbon nanotube doped phosphor nanocomposite for ultra bright electroluminescence

The effective doping of multi-walled carbon nanotube (CNT) in the ZnS:Cu phosphor nanocomposite and thereafter improvement in the optical performance of electroluminescent (EL) device due to increased local eld effects has been studied in detail. To facilitate doping of CNTs into the phosphor and decrease the operating voltage of the EL device, CNTs were shortened by milling and incorporated effectively using a flux assisted solid-state annealing reaction. Interestingly shorter the length of CNTs used; greater was the local field enhancement, improvement in brightness and efficiencies observed for the EL devices. When the field is applied, adequate charge carriers are tunneled into the ZnS:Cu system through the tips of the CNTs by forming high energy hot spots thus enhancing the local field. The improved device characteristics are due to field enhancement and effective transfer of energy from hot spots to copper activator by impact ionization. The detailed electrical characterization of the novel EL device

Fig. 2.25: Confocal fluorescence image of thin films of (i) YVO₄:Eu⁴⁺ (ii) YVO₄:Eu³⁺ + 22nm Ag nanopism combine (iii) YVO₄:Eu³⁺ + 45nm Ag nanopism combine (iv) TEM images of Ag nanopism (v) schematic of arrangements of YVO₄:Eu³⁺ NPs (red spheres), PVA layer (yellow transparent layer) and Ag NPs (blue prisms) in thin films used for study, (vi) integrated fluorescence spectra of the samples under 980nm laser excitation taken by Confocal fluorescence measurements. Simulated near field images of single Ag nanoproms (22 nm and 45 nm) and dimers calculated by FDTD method, by importing exact TEM image of Ag NP
Fig. 2.26 (a): Variation of current density (J) as a function of applied field (E) for the AC driven EL device; first inset shows change in the current efficiency of the EL device as a function of applied voltage; second inset shows the photograph of the working device at an operating voltage of 100 V$_{Ac}$ and 2.5 kHz. (b) Scheme showing band bending model due to incorporation of CNTs presented (Fig. 2.26) by considering the hot electron injection model.

**Multifold blue absorption of a new red-emitting nanophosphor for LEDs**

There has been a stringent demand for blue (~450 to 470 nm) absorbing and red (~611 nm) emitting material systems in phosphor converted white light emitting diodes (WLEDs) available in the market. The conventionally used red-emitting Y$_2$O$_3$:Eu$^{3+}$ phosphor has negligible absorption for blue light produced by GaInN based LED chips. To address this issue, a new red-emitting Gd$_2$CaZnO$_6$:Eu$^{3+}$ (GCZO:Eu$^{3+}$) nanophosphor system having exceptionally strong absorption for blue (~465 nm) and significant red (~611 nm) photoluminescence is presented (Fig. 2.27). This is attributed to a dominant f-f transition ($^5D_{0}/^7F_{2}$) of Eu$^{3+}$ ions, arising due to an efficient energy transfer from the Gd sites of the host lattice to Eu$^{3+}$ ions. The external quantum yield (QY) measured at 465 nm absorption and 611 nm emission revealed that

Fig. 2.27: Photoluminescence excitation (PLE) of (a) commercial Y$_2$O$_3$:Eu$^{3+}$ phosphor, (b) GCZO:Eu$^{3+}$ microcrystalline bulk phosphor, (c) GCZO:Eu$^{3+}$ nanophosphor monitored at ~611 nm emission. The dotted region depicts the multifold blue light absorption at ~465 nm for GCZO:Eu$^{3+}$ and (d) magnified version of the same, useful for improving color rendering in WLEDs
the GCZO:Eu³⁺ nanophosphor has better QY of 23% as compared to commercial Y₂O₃:Eu³⁺, which is <1%. X-ray diffraction and microscopy observations showed the nanocrystalline nature and slightly elongated morphology of the sample, respectively. While the energy dispersive X-ray analysis identified the chemical constituents of the GCZO:Eu³⁺ nanophosphor, the color overlay imaging confirmed the substitution of Eu³⁺ for Gd³⁺ ions. As seen from the QY statistics it is highly anticipated that the multifold absorption at ~465 nm would certainly improve the color rendering properties of existing WLEDs.

**Probing on lanthanide doped nanophosphor as a broad spectral converter (UV-IR) for promising next generation Si-solar cell**

Recent thrust in the research activity of lanthanide doped nanomaterials have been largely attributed to its fascinating properties and its vast potential applications in display technology, optoelectronics, bio-imaging, and for security applications. The current focus in this field is to develop efficient luminescent materials for enhancing the efficiency of Si-solar cells via modification of the solar spectrum response. Lanthanide ions are the primary entities to achieve efficient spectral conversion. Because of their rich energy level structure and lanthanide can accomplish both down-shifting (DS) and up-conversion (UC) processes which may allow for facile photon management. Our main objective is to make an attempt to synthesize nanophosphors which can absorb UV-IR region and may be modify as well as convert the solar spectrum into beneficial energy with high efficiency.

We have successfully demonstrated the synthesis of highly luminescent DS and UC Gd₃(MoO₄)₂:RE nanophosphor by solid state reaction which can be scale up in pilot plant. The as-synthesized luminescent DS Gd₃(MoO₄)₂:Eu³⁺

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Fig. 2.28: photoluminescence excitation spectrum of Gd₃(MoO₄)₂:Eu³⁺ DS nanophosphor at emission 623nm emission wavelength, (b) photoluminescence emission spectrum of Gd₃(MoO₄)₂:Eu³⁺ DS nanophosphor at emission 395nm excitation wavelength, (c) photoluminescence emission spectrum at excitation 980nm and (d) photoluminescence emission spectrum of UP Gd₃(MoO₄)₂:RE (Er³⁺,Yb³⁺) phosphor at excitation 1550 nm.
nanophosphor exhibits excitable at 291, 362, 377, 385, 416, and 465nm with strong red emission peaking at 623nm wavelength as shown in Figure 2.28 (a & b). The as-synthesized luminescent UC Gd₂(MoO₄)₃:Er³⁺,Yb³⁺ nanophosphor exhibits excitable at 980 and 1550nm with emission peaks at 542 and 977 nm wavelength as shown in Figure 2.28 (c & d). The obtained Photoluminescent results confirms the full utility of Gd₂(MoO₄)₃:RE (Eu, Er, Yb) nanophosphor as a Broad Spectral converter (UV-IR) for promising Next Generation Si-Solar Cell.

**Multiferroics and Magnetics**

**Magnetic Metrology**

Calibration and Test activities for R&D institutions & industrial instruments have been undertaken and 61 calibration/test reports were issued, this led to Rs.7.8 Lakh of ECF earning.

A calibration methodology for precise NMR Teslameter by using High Resolution Frequency counter has been developed and achieved uncertainty of 35 μT/T in the measurement range of 0.043T-1.0T.

As an special initiative we have successfully installed our Cesium Magnetometer (as Primary standard for low magnetic field measurement facility) with an uncertainty of 10nT/T for 20,000 nT-1,00,000 nT magnetic field range. Lot of efforts have been put to improve uncertainty for low magnetic field measurement ranges.

For the first time an onsite survey has been successfully initiated for electromagnetic radiation measurement, calibration of ELF/EMF Meters.

The best possible efforts are being tried out to improve further uncertainty of measurement to provide best calibration/test results with minimum probable error. Our group provides solution to industrial problems.

**Colossal Humi-do Resistance, CHR, in ceria added magnesium ferrite thin film by pulsed laser deposition**

First time, magnesium ferrite and ceria added magnesium ferrite thin films have been prepared by Pulsed laser deposition technique. Pure magnesium ferrite showed decrease in resistance from 230 GOhm at 10%RH to 184 MOhm at 95%RH. While 1 wt% Ce:MgF thin film resistance was 1.8 TOhm at 10% RH which deceased to 754 KOhm at 95 %RH exhibiting approximately a seven-order decrease in the resistance (Fig. 2.29). The DC resistance of pure magnesium ferrite film was 256 GOhm at 0 %RH.

![Image](image-url)

**Fig. 2.29:** (a) InR vs. % relative humidity plot for thin films showing change in resistance with humidity and (b) humidity sensing mechanism by film.
humidoresistance based devices contrary to colossal magnetoresistance (CMR) devices operated by externally applied magnetic field. A comparison between GMR & CHR is shown below in Table 2.2. It is evident from the impedance plots that in dry atmosphere (0%RH) InZ of the films decreased linearly with increasing frequency exhibiting material transport characteristics (Fig. 2.30). When films exposed to humidity, initial drastic decrease in impedance of films by humidity is due to conduction of $H_2O^+$ and $H^+$ ions in physisorbed water molecules via hydrogen bonding at low frequency on the surface of films. The constant region extended at higher 90% RH compared to lower 10%RH due to increased $H_2O^+$ ions concentration at higher humidity. This exhibits conduction contribution is due to very low concentration of free $H_2O^+$ ions.

Table 2.2

<table>
<thead>
<tr>
<th>GMR (giant magneto-resistance)</th>
<th>CHR (colossal humido-resistance)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multilayer is required</td>
<td>Single layer is required</td>
</tr>
<tr>
<td>Thickness of each layer is critical</td>
<td>Thickness is not below 60 nm</td>
</tr>
<tr>
<td>Very High External Magnetic Field is Needed</td>
<td>Natural Source relative Humidity is Needed</td>
</tr>
<tr>
<td>Change in %MR is 0.7-1/Oe</td>
<td>Change in resistance is 0.1 Mohm/1%RH</td>
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Spin pumping induced Spin Hall Effect on Co/Pt bilayer thin film

Spin pumping induced spin-Hall effect has been investigated in RF sputtered Co/Pt bilayer thin film for its application in the field of spintronics. Microwave power has been applied in presence of a magnetic field and measured the FMR voltage spectra across the film. Schematic illustrations of flow of spin current $J_s$ and charge current $J_c$ in Co/Pt bilayer thin film on Si substrate is shown in Fig 2.31.

Fig. 2.31: Schematic illustrations of flow of spin current $J_s$ and charge current $J_c$ in Co/Pt bilayer thin film on Si substrate
The saturation magnetization of the Co/Pt bilayer thin film was measured as $0.55 \times 10^3$ emu/cm$^3$ when the applied magnetic field was kept perpendicular and $0.32 \times 10^3$ emu/cm$^3$ for parallel magnetic field with respect to film plane. It exhibits film is perpendicularly anisotropic (Fig. 2.32). The FMR signal was excited by a microwave signal, while applying sweeping dc magnetic field along and perpendicular to the film plane separately. The maximum dc voltage measured was 5.78 V at 0.1GHz in perpendicular applied magnetic field on the bilayer (Fig. 2.33).

**Fig. 2.32:** Schematic illustrations of flow of spin current $J_s$ and charge current $J_\text{m}$ in Co/Pt bilayer thin film on Si substrate

**Induced magnetism and magnetoelastic coupling in ferroelectric BaTiO$_3$ by Cr-doping synthesized by facile chemical route**

Phase pure barium titanate (BTO) and Cr-doped BTO have been synthesized by a facile single-step metal-organic decomposition (MOD) method. Ferroelectric transition temperature value for pure BTO is decreased to 108 $^\circ$C by 1.5 Cr doping in BTO due to tetragonal to distorted cubic structural change (Fig. 2.34). Diamagnetism of BTO transformed into ferromagnetic behaviour by Cr-doping on the expense of decrease in polarization. The ME coupling coefficient of 1.5 Cr:BTO at room temperature maximum value of $\alpha$ obtained is 13 mV cm$^{-1}$Oe$^{-1}$ for 2800 Oe (Fig. 2.35).

**Fig. 2.34:** Ferroelectric transition temperature of pure BTO and 1.5Cr:BTO at different frequencies

**Fig. 2.33:** Maximum dc voltage generated is 5.78 V at 0.1 GHz
Magnetoelectric Coupling of Multiferroic Chromium Doped Barium Titanate Thin Film Probed by Magneto-Impedance Spectroscopy

Thin film of $\text{BaTiO}_3$ doped with 0.1 at% Cr (Cr:BTO) has been prepared by Pulsed laser deposition technique for the first time. A smooth platform of uniform color of film reveals smooth growth of thin film. The magnetic domains recorded in the MFM image are clearly visible in the form of alternating dark and bright contrast fringes, exhibiting strong and weak magnetic force on MFM tip. The size of the domain in this is about 1-2 $\mu$m in width. MFM images qualitatively further supports the quantitative magnetization of ferroelectric film obtained by MH loop (Fig. 2.36). Theoretical impedance equation fitted to experimental data in Cole-Cole plot for thin film (Fig. 2.37) in presence of transverse magnetic field resolved the increase in grain capacitance from $4.58 \times 10^{-12}$ to $5.4 \times 10^{-11}$ F. Ten times higher ME coupling coefficient 137 mV/cm than bulk value of 13 mV/cm has been obtained even at lower applied magnetic field 1000 Oe (Fig. 2.38).

Magnetoelectric coupling-induced anisotropy in multiferroic nanocomposite (1-x) $\text{BiFeO}_3$–x$\text{BaTiO}_3$

Nanocomposite (1 –x)$\text{BiFeO}_3$–x$\text{BaTiO}_3$ for x = 0.1, 0.2 and 0.3 has been investigated for magnetoelectric (ME) coupling at atomic scale mixing of the two phases. XRD results revealed
Fig. 2.36: (a) M (Magnetic moment) vs. H (Magnetic field) loop for Cr:BT0 thin film, (b) Room temperature AFM image and (c) the corresponding MFM image of the Cr:BT0 film taken on the scale of 15 µm

Fig. 2.37: Impedance spectroscopy plot Z'' vs. Z' at zero and 5 KOe magnetic field and theoretical plot fitting to experimentally observed curves, inset shows close view fitting of theoretical plot on two curves

Fig. 2.38: Induced voltage per unit AC field and film thickness with applied DC bias magnetic field

Fig. 2.39: Comparison of XRD results of nanocomposite (1-x) BiFeO₃-xBaTiO₃ for x = 0, 0.1, 0.2 and 0.3, inset (a) shows (100) peak shifting towards lower angle representing increasing lattice parameter and inset (b) shows disappearance of splitting of (110) peak representing phase transition from rhombohedral to cubic structure
dielectric maximum was found to be at 395°C for 10 kHz for x= 0.1 (Fig. 2.40) which shifted to 450°C at 1 MHz. Dielectric maximum ME coupling coefficient (d) was maximum 2.74 mV/cmOe for x = 0.1.

Biomedical Instrumentation

The Biomedical Instrumentation section has successfully established a DST center for biomolecular electronics under a DST funded project. The section has also established two prototype devices for detection of total cholesterol. This section is dedicated to research in both pure and applied science and integrated research field involving the principles of Physics, Chemistry, Biotechnology and Instrumentation with the following objectives:

- To focus on R & D in controlled target- drug delivery, diagnostics and therapeutics based on smart inorganic and organic materials, conducting polymers, nanomaterials and biocompatible materials for bioelectronics devices, biomedical sensors and innovative technologies
- Developing, identifying and building new information and knowledge based strategies for generating new materials for molecular electronic applications such as conducting polymers, self-assembled monolayers, nanophosphors, sol-gel films, Langmuir Blodgett monolayer films etc
- Fabricate on-line, in-situ and ultimately non-invasive tools of diagnostic devices
- Highly specific, sensitive and selective polymeric multivariate biosensor, whole cell biosensor for pesticides/heavy metal detection etc
- Nucleic acid hybridization biosensors for microbial detection
- Technological development of novel devices, processes and methodologies, and transfer of technical expertise for pilot production of biomedical sensors
- To generate and supplement technical manpower in the area of biosensors and biomolecular and molecular electronics
- Generate high quality research papers and patents
- Transfer of technical know-how on molecular electronics devices to pertinent industries

The group has also undertaken the integrated M. Tech.-Ph.D./ Ph.D. programme on biosensors under Academy of Scientific and Innovative Research (AoSIR) and other collaborative academic institutes.

Some of the research highlights for detection of Escherichia coli, Cholesterol and LDL, using various non conventional approaches, such as, liquid crystals cell and microfluidics cells have been used for detection of cholesterol also novel material such as Cationic poly (lactic-co-glycolic acid) iron oxide nanosphere as nucleic acid sensors.

Cationic poly (lactic-co-glycolic acid) iron oxide microspheres for nucleic acid detection

Herein, we envisage the possibility of preparing stable cationic poly (lactic-co-glycolic acid) (PLGA) microspheres encapsulating the iron oxide nanoparticles (IONPs; 8–12 nm). The IONPs are incorporated into PLGA in organic phase followed by microsphere formation and chitosan coating in aqueous medium via nano-emulsion technique. The average size of the microspheres, as determined by dynamic light scattering are about 310 nm, while the zeta potential for the composite
remains near 35 mV at pH 4.0. These microspheres are electrophoretically deposited on to indium tin oxide (ITO)-coated glass substrate used as cathode and parallel platinum plate as the counter electrode. This platform is utilized to fabricate a DNA biosensor, by immobilizing a probe sequence specific to Escherichia coli. The bioelectrode shows a surface-controlled electrode reaction with the electron transfer coefficient ($\alpha$) of 0.64 and charge transfer rate constant ($k_s$) of 61.73 s$^{-1}$. Under the optimal conditions, this biosensor shows a detection limit of $8.7 \times 10^{-7}$ M and is found to retain about 81% of the initial activity after 9 cycles of use.

**Electrochemically Assembled Gold Nanostructures Platform: Electrochemistry, Kinetic Analysis, and Biomedical Application**

A novel one-step electrochemical method for controlled synthesis of electroactive gold nanoparticles (Au NPs) in an organic medium using an organometallic precursor Au(PPh$_3$)$_3$Cl ($Ph = \text{phenyl}$) has been proposed. The hierarchical assembly of Au nanostructures has been tuned on indium tin oxide (ITO) surface during electrochemical reduction of Au(PPh$_3$)$_3$Cl using cysteamine. The Au NPs act as building blocks to form secondary structures of Au that has been confirmed using transmission electron microscopic studies. The presence of triphenylphosphine in Au film enhances the electrocatalytic activity, resulting in higher charge transfer kinetics. The cholesterol oxidase (ChOx) as a model enzyme has been immobilized on various fabricated nanostructured Au films. Direct electron transfer properties of nanostructured Au films result in third-generation cholesterol biosensor. We have investigated the biosensing performance of different Au nanostructures toward cholesterol estimation at low operating potential (+0.3 V). The high sensitivity of 4.22 AM$^{-1}$ cm$^{-2}$ and low detection limit of 5.49 µM of this biosensor (ChOx-Glu/Cys-Au/ITO) is due to higher current resulting from monodisperse Au NPs. In addition, this bioelectrode shows charge transfer rate constant as 247.27 s$^{-1}$ and low $K_{m}^{app}$ value as 0.57 mM. The biosensor shows good reproducibility, stability, and selectivity and thus can be utilized for health care diagnostics application.

**Protein-Conjugated Quantum Dots Interface: Binding Kinetics and Label-Free Lipid Detection**

We propose a label-free biosensor platform to investigate the binding kinetics using antigen–antibody interaction via electrochemical and surface plasmon resonance (SPR) techniques. The l-cysteine in situ capped cadmium sulfide (CdS; size < 7 nm) quantum dots (QDs) self-assembled on gold (Au) coated glass electrode have been covalently functionalized with apolipoprotein B-100 antibodies (AAB). This protein conjugated QDs-based electrode (AAB/CysCdS/Au) has been used to detect lipid (low density lipoprotein, LDL) biomolecules. The electrochemical impedimetric response of the AAB/CysCdS/Au biosensor shows higher sensitivity (32.8 kΩ µM$^{-1}$/cm$^3$) in the detection range, 5–120 mg/dl. Besides this, efforts have been made to investigate the kinetics of antigen–antibody interactions at the CysCdS surface. The label-free SPR response of AAB/CysCdS/Au biosensor exhibits highly specific interaction to protein (LDL) with association constant of 33.4 kM$^{-1}$ s$^{-1}$ indicating higher affinity toward LDL biomolecules and a dissociation constant of 0.896 ms$^{-1}$. The results of these studies prove the efficacy of the CysCdS-Au platform as a high throughput compact biosensing device for investigating biomolecular interactions.

**Metals & Alloys**

**Thermoelectric material Cu$_3$SbSe$_3$ with intrinsically ultralow lattice thermal conductivity**

This is the first comprehensive study on the synthesis, characterization and thermoelectric property evaluation of Cu$_3$SbSe$_3$ synthesized using a single-step process employing a solid-state reaction in vacuum. The synthesized material was
p-type behavior in the measured temperature range of 300-550 K and exhibits a order-disorder transition at ~ 450 K, which has also been reported earlier. Electronic band structure of Cu$_3$SbSe$_3$ has been evaluated using first-principle density functional theory (DFT) calculations and the electrical transport properties were theoretically evaluated using Boltzmann transport theory (Fig. 2.42). These theoretical predicted values of thermopower (S) and electrical conductivity (σ) were found to be in reasonable agreement with the experimental results. The measured thermal conductivity (κ) was found to be 0.26 Wm$^{-2}$K$^{-1}$ (550 K), which is the lowest value reported for this material thus far and is among the lowest for thermoelectric materials. However, despite a ultralow κ and moderate S, the calculated thermoelectric figure-of-merit was abysmally low, which is due to very low σ. Thus, it has been experimentally established for the first time that pristine Cu$_3$SbSe$_3$ is not a good thermoelectric material, which is contrary to the previously reported proposition. Nevertheless, it is suggested that this material could be a good potential thermoelectric material owing to its ultralow κ coupled with a reasonable value of α, as σ can be tailored favorably by employing suitable metallic doping.

Fig. 2.41: Temperature dependence of transport properties of Cu$_3$SbSe$_3$. The open circles represent the experimental points and the coloured lines depict the theoretically predicted curves, for different carrier concentration. (a) Seebeck coefficient. (b) electrical conductivity (c) total thermal conductivity. The inset shows the temperature dependence of specific heat characterized for its structure and composition employing X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDXS) X-ray photoemission spectroscopy (XPS) and differential scanning calorimeter (DSC). These detailed characterization results clearly confirmed the formation Cu$_3$SbSe$_3$ in a single phase.

The electrical transport measurement results (Fig. 2.41) indicated that, contrary to the earlier theoretical prediction, Cu$_3$SbSe$_3$ exhibits a
Fig. 2.43: Seeback coefficient of figure-of-merit of (a) n-type Mg₃Si and (b) p-type MnSi₇.

Development of cost effective Mg₃Si Based thermoelectric material

Silicides are being considered as potential TE materials and have been the focus of research for the past about five years. Silicides are one of the cheapest elements compared to constituent elements of conventional thermoelectric materials. We have synthesized both n-type Mg₃Si and p-type MnSi₇ successfully, via milling using high energy ball milling followed by reaction sintering employing spark plasma sintering (SPS). Fig. 2.43 shows the Seebeck coefficient and figure-of-merit compatibility of these synthesized p & n-type materials.

Enhanced Thermoelectric Performance of a new half-Heusler Derivative Zr₉Ni₇Sn₈ Bulk Nanocomposite

Varying valence electron concentration per unit cell (VEC) in half-Heusler (HH) derives a large number of structures and substructures which can be exploited to improve the thermoelectric performance of HH. Herein, we report Zr₉Ni₇Sn₈ having VEC of 17.25 per formula unit which is off-stoichiometric HH ZrNiSn for thermoelectric applications. The structural analysis employing XRD, SEM and TEM (Fig. 2.44) confirms the resulting material to be a composite of HH and Ni₃Sn₄-type phases. Rietveld analysis estimates the...
volume fraction of HH to be $75.6 \pm 1.2\%$ and $24.6 \pm 0.8\%$ for Ni$_3$Sn$_4$ phase. Interestingly, the present composite results in substantial increase in electrical conductivity ($\sigma$) by $\sim 75\%$ and a drastic reduction in thermal conductivity ($\kappa$) by $\sim 56\%$, leading to a thermoelectric figure of merit (ZT) of $0.38$ at $773K$, which is $\sim 87\%$ higher than in normal HH ZrNiSn (Fig. 2.45). Further, the nanostructuring of the composite, employed by in mechanical milling, derives to a significantly reduced $\kappa$ (i.e. from $4.56W/mK$ to $3.36W/mK$, at $323K$), yielding to a ZT of $0.90$ at $773K$, which is $>300\%$ enhancement over the normal HH. The experimental results have been compared with the Bergman and Fel model for calculating effective thermoelectric parameters in composites. The results obtained in the present work motivate to design in-situ bulk composite consisting of HH and metallic inclusions Ni$_3$Sn$_4$ in an off-stoichiometric HH composite with VEC smaller than 18 for drastic reduction in $\kappa$ and simultaneous improvement in the electrical transport.

Role of nanoscale features in enhancing the thermoelectric performance of spark plasma sintered nanostructured p-type SiGe alloy

Nanostructured p-type Si$_{80}$Ge$_{20}$ alloy synthesized employing high energy ball milling followed by spark plasma sintering (SPS) after optimizing the process parameters. X-ray diffraction pattern of the ball milled powder showed the crystallite size was $\sim 14$ nm and further coarsened up to $\sim 22$ nm after spark plasma sintering (SPS). The rapid-heating rates associated with SPS resulted in a densification of 97.3%, while retaining the nanostructured features, which was obtained after ball-milling. Thermal conductivity of nanostructured Si$_{80}$Ge$_{20}$ alloy after SPS has been measured to be 2 W/mK at 900°C which is 22% less than the best reported value so far. The reduced thermal conductivity was mainly due to the increased interfaces consisting of randomly distributed high angle grain boundaries with atomic defects or disorders (TEM in Fig. 2.46). Also, the FESEM analysis of sintered alloy confirmed the

![Fig. 2.45: Temperature dependence of thermoelectric properties of ZrNiSn normal HH, Zr$_2$Ni$_3$Sn$_4$ bulk composite (BC), Zr$_2$Ni$_3$Sn$_4$ bulk nanocomposite (BNC), Ni$_3$Sn$_4$ [in inset] and calculated effective thermoelectric parameters for composite using Bergmen & Fel model (a) electrical conductivity (b) Seebeck coefficient (c) power factor (d) total thermal conductivity (e) lattice and electronic thermal conductivity (f) calculated thermoelectric figure of merit](image1)

![Fig. 2.46: Temperature dependence of thermoelectric properties of ZrNiSn normal HH, Zr$_2$Ni$_3$Sn$_4$ bulk composite (BC), Zr$_2$Ni$_3$Sn$_4$ bulk nanocomposite (BNC), Ni$_3$Sn$_4$ [in inset] and calculated effective thermoelectric parameters for composite using Bergmen & Fel model (a) electrical conductivity (b) Seebeck coefficient (c) power factor (d) total thermal conductivity (e) lattice and electronic thermal conductivity (f) calculated thermoelectric figure of merit](image2)
Fig. 2.47: Temperature dependence of thermoelectric properties of sintered p-type Si$_{50}$Ge$_{50}$ nanostructured alloys (a) Electrical conductivity  (b) Seebeck coefficient (c) Total thermal conductivities (d) Lattice thermal conductivity comparison with other SiGe alloys available in literature (d) figure-of-merit and its comparison with those reported in literature.

The heterogeneous distribution of nano-sized pores of size 25 to 150 nm within the matrix. Further, high HRTEM observations confirmed the post sintering nanoscale features with large density of interfaces. Finally, the significant reduction in thermal conductivity without scarifying the electrical conductivity resulted in considerable enhancement of ZT about $\pm 1.2$ at 900 °C (Fig. 2.47), which is a 26% higher value to that of best reported for p-type Si$_{50}$Ge$_{50}$ alloys.

**Synthesis of Rare Earth free Permanent Magnetic Materials**

The main objective of this activity is to synthesis Rare-Earth Free Permanent Magnetic Material e.g. MnAl, Mn-Bi-Fe, manganese antimonide etc. employing arc melting, Melt spinning, conventional melting, high energy ball milling and spark plasma sintering techniques. Efforts have been made to synthesize single-phase MnBiFe alloy essentially using melt spinning technique and annealing. As melt spun MnBiFe alloy gives better properties than as arc melted alloy. Optimization of annealing parameter by controlling annealing temperature and time resulted in a BHmax around 2MG0e (Fig. 2.48).

Fig. 2.48: M-H curves of MnBiFe with synthesized using different processing methods and annealing conditions

**Development of Aluminum alloy-Carbon Nanotubes (Al-CNTs) composites employing Cryomilling and hot extrusion**

One of the major challenges towards the development of Al-CNTs and similar metal matrix composites is achieving a uniform dispersion of CNTs in the metal matrix, since Vander Wall forces cause agglomeration of CNTs during mechanical alloying with metal powder. The research on the development of high strength-light weight Al-CNTs composites has been initiated with the support of CSIR-NPL. In this activity, the powder mix of pure Al alloy and MWCNTs (0.5 wt.%) was obtained by solution dispersion method, which was milled in liquid N$_2$ using a cryomilling attritor. Different parameters, such as ball to powder ratio and milling time were varied keeping milling speed as fixed as 240 rpm. For the balls to powder weight ratio of 20:1 and milling time of 2 h, a uniform dispersion of CNTs in the Al matrix was obtained (shown in Fig 2.49a). The cryomilled pure Al-CNTs powder was consolidated by (i) cold pressing at $\sim$400 MPa followed by sintering under vacuum at $\sim$550 °C and
Fig. 2.49: (a) SEM micrograph of cryomilled Al-MWCNTs (0.5 wt%) composite powder showing a uniform dispersion of CNTs in the aluminum matrix and (b) Photograph of the hot extruded Al-0.5 wt% MWCNTs rod [close-up view in (b) shown in inset represents defect-free lustrous surface]

(ii) pre-compacted followed by hot extrusion at 400°C at an extrusion ratio of 15 so as to develop rods of 12 mm dia (Fig. 2.49b). The pure Al-0.5% CNTs composite powder has delivered tensile strength and Vickers microhardness of ~35 MPa and 32 HV<sub>200</sub>, respectively, which has been enhanced to >200 MPa and 72 HV<sub>200</sub> respectively after hot extrusion.