-CHAPTER II

LITERATURE REVIEW AND SCOPE OF THE PRESENT WORK

2.1 Literature Review

2.1.1 Review of copper iodide nanoparticles

Mohd Rafie Johan et.al (2012), have prepared Polycrystalline CuI nanoparticles via convenient liquid-phase route from the Cu^{+} - DMF solution precursor. A passivation layer of Cu^{+} -DMF absorbed on the particle surface were responsible for the nanoparticles formation. The broadening of XRD patterns showed that the size of CuI particle is reduced. The TEM image showed the spherical and well-dispersed of CuI nanoparticles.

A new technique for the preparation of CuI nanoparticles from CuSO4 and KI ethanol solutions has been developed by Hong Tao Li and Li Xia Gu (2007). Preparation conditions were optimized through a series of experiments. Under these conditions, the yield of CuI reached 95.39%. The product was characterized and the reaction kinetics was studied.

A new technique for the preparation of CuI nanoparticles from CuSO4 and KI ethanol solutions has been developed by Jalal Albadi et.al (2013), have synthesised Poly(4-vinylpyridine)-supported nanoparticles of copper(I) iodide as a new, efficient and recyclable catalyst for the synthesis of 1,8-dioxooctahydroxanthenes under solvent-free conditions. This catalyst was recovered by simple filtration and recycled up to 10 consecutive runs without losing of its efficiency.

Cuprous iodide nanoparticles was successfully synthesized with a rapid, low cost, one pot and solvent free reaction using the mechanochemical method by Saeed Shahbazi and Shahrara Afshar (2014). The XRD EDX analysis, SEM images and diffuse reflectance spectrum (DRS) of the product showed the successful synthesis of pure cuprous iodide (CuI) nanoparticles.

Uday V. Desaiet.al (2014) have prepared cellulose supported cuprous iodide nanoparticles (Cell-CuI NPs) for the first time as an efficient heterogeneous catalyst in the click synthesis of 1,4-disubstituted 1,2,3-triazoles by a one-pot three component reaction between aralkyl/alkyl bromides, alkynes and sodium azide in water. The catalyst has been characterized by XRD, HRTEM, SEM, ICP–AES, EDS as well as IR spectroscopy.

ZarrinGhasemi et.al (2016) have synthesised and characterized a highly active catalyst based on copper iodide nanoparticles supported on magnetic aminomethylpyridine functionalized cellulose. Its catalytic activity was investigated in the multicomponent synthesis of N-sulfonylamidines via an in situ generated sulfonylketenimine intermediate under solvent free conditions at room temperature. The desired products were obtained in good to excellent yields at short reaction times.

A simple and efficient synthesis of pyrimido[b]quinolinetriones is introduced using copper (I) iodide nanoparticles (CuI NPs) as an efficient heterogeneous catalyst in green media-water by ShahrzadAbdolmohammadi and Zahra Aghaei-Meybodi (2015). The catalyst was prepared through the simple precipitation route and well characterized by various techniques such as XRD and SEM. The mild reaction conditions, using aqueous medium, reusability of the catalyst, simple reaction work-up and excellent yields of products make the present protocol sustainable and advantageous compared to the conventional methods.

N. Shionoiri et.al (2012), have demonstrated the antiviral properties of copper iodide (CuI) nanoparticles against the non-enveloped virus feline calicivirus (FCV) as a surrogate for human norovirus. The effect of CuI nanoparticles on FCV infectivity to Crandell-Rees feline kidney (CRFK) cells was elucidated. The infectivity of FCV to CRFK cells was greatly reduced by 7 orders of magnitude at 1000 μgml(-1) CuI nanoparticles.

A. Pramanik et.al (2012), have synthesised CuI nano particles by co-precipitation method with an average size of 8 nm as determined by Transmission Electron Microscope (TEM). The average charge of the NPs is -21.5 mV at pH 7 as obtained by zeta potential measurement and purity is determined by XRD. These NPs are able to kill both gram positive and gram negative bacteria.

Cuprous iodide (CuI), that has been recently used as an inorganic hole-conductor material in perovskite solar cells, was successfully synthesized by Mahdi Malekshahi Byranvand and Ali NematiKharat (2014) with a green, rapid, low cost and room temperature method. Sugar beet juice was used as a reductant and capping agent, because of the presence of anthocyanin molecules in its ingredients. By using different amounts of juice, various morphologies of CuI have been obtained.

J. Safaei-Ghomi et.al (2012), have studied that CuI nanoparticles acts as an expedient and recyclable catalyst for the synthesis of N-cyclohexyl-3-aryl-quinoxaline-2-amines in ethanol via a multi-component reaction. The products were separated from the catalyst simply by filtration. The catalyst could be recycled and reused for several times without noticeably decreasing the catalytic activity.

Mohammad Ali Ghasemzadeh et.al (2016) have developed novel application of copper iodide nanoparticles as an efficient catalyst for the synthesis of 2,3-disubstituted benzo[b]furan derivatives via three-component coupling of aldehydes, secondary amines and alkyne. The method presented is green, effective, inexpensive and satisfactory to give the products in high yields and short reaction times by the use of novel nanoscale materials.

Copper iodide nanoparticles (NPs) are reported for the reductive amination of carbonyl compounds by Rajaram Ba et.al (2017). The generated NPs were characterized by TEM, EDX, XRD and XPS analyses. The XRD patterns, XPS, and EDX analysis confirmed that the

resulting NPs were CuI instead of Cu. The TEM images of CuI exhibited the size of monodispersed spherical NPs in the range of 4 ± 2 nm. These generated NPs can be used as versatile heterogeneous catalysts for important organic transformations.

H. Hernández-Cocoletzi et.al (2009), have performed first principles total energy calculations to investigate the structural properties of copper iodide (CuI) in its sodium chloride, cesium chloride, zinc blende and wurtzite structures. Calculations are done using the density functional theory. Optical absorption experiments and X-ray diffraction measurements have shown that zinc blende is the ground state of CuI. Our calculations find that in the GGA formalism wurtzite and zinc blende have similar total energies. Results show that the energy difference between the wurtzite and the zinc blende structures, as calculated within the GGA formalism is 2 meV. At higher pressures it is possible to have a phase transition to the CsCl geometry.

CuI nanoparticles were fabricated from conventional CuI powders in micrometer size by Keisaku Kimura et.al (2005). Acetonitrile was used as a dispersing agent to dissolve CuI powders. With acetonitrile evaporated, poly-2-vinylpyrolidine (PVP) in the solution could effectively restrict CuI particle growth, prevent them from aggregation, and result in the formation of CuI nanoparticles embedded in the polymer matrix.

2.1.2 Review of Copper iodide thin films

R.N.Bulakheet.al (2013), have reported the structural, morphological, electrical studies of copper iodide (CuI) thin films deposited onto glass substrates by chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) methods. CuI thin films were characterized for their structural, morphological and wettability studies by means of X-ray diffraction, FT-Raman spectroscopy, scanning electron microscopy, optical absorption and contact angle measurement methods.

The technique of laser-assisted molecular-beam deposition (LAMBD) has been used by W. M. K. P. Wijekoon et.al (1993), to fabricate a molecular film by reaction in a molecular beam. Molecular iodine vapor entrained into a stream of helium carrier gas was introduced via a supersonic expansion into the plasma plume of laser-evaporated copper to produce copper iodide. Films were deposited on substrates that were situated about 3 cm downstream on the path of the molecular beam.

A chemical method for preparing CuI thin films by iodination of solution grown Cu_2S films is described by Tapas Chaudhuri et.al (1990). X-ray characterization identifies γ-CuI and suggests that the films are polycrystalline in nature. SEM reveals granular film morphology. Optical studies show that the band gap of the material is 2.93 eV.

F.Iskandar et.al (2016), have developed a synthesis method for CuI thin film with in-situ spraying, a low cost, safe and easy fabrication method. As precursor solution, CuSO4·5H2O was dissolved in ammonia and KI aqueous solution. The precursor solution was then sprayed directly onto a glass substrate with appropriate temperature to form CuI film. The prepared thin films were characterized by X-ray diffractometer, UV-Vis spectrophotometer, scanning electron microscope and four-point probes to study their properties.

Chang-Ho Choi et.al (2016),have fabricated p-type CuI TFTs by printing molecular CuI ink directly onto the device substrate followed by immediate crystallization of CuI nanoparticles as the solvent evaporated. The substrate temperature during inkjet printing was varied in order to obtain continuous CuI films with large grain size for improved device performance.

The transparent semiconducting copper iodide (CuI) films were deposited by pulsed laser deposition (PLD) and their structural and opto electrical properties in the power output of TiO_2|Dye|CuI cells are reported by M. Rusop et.al (2004). These CuI films exhibited optical

transmittance of over 80% in the wavelength range from 400 to 900 nm and a minimum resistivity of about 2 KΩ-cm.

M. Amalina and Teknologi(2012), have studied the effect of molar concentration of *CuI* thin film deposited by mist atomization technique. The result shows the *CuI* thin film properties strongly depends on its precursor concentration. Thickness between 0.35 x 10^4 nm - 1.60 x 10^4 nm was obtained as the concentration increases. The increment of thickness affects the electrical properties which is the resistivity and conductivity of *CuI* thin film.

KiseokJeon et.al (2018), have fabricated CuI thin films with wide band gaps and large work functions on n-type silicon substrates via a thermal evaporation technique. Changes that take place in the structural, morphological and optical properties of CuI thin films based on different thicknesses (11 to 58 nm) were analyzed. X-ray diffraction patterns reveal that poly crystalline CuI thin films a have γ-phase with preferential growth in the (111) direction. Increases in the peak intensity for the (111) diffraction plane were observed in the thicker films. Generally, deposited CuI films exhibit triangular shapes with azimuthal orientation but these shapes disappeared as the film thickness was increased.

Fabian I. Ezema et.al (2017) have studied that the addition of impurities, method of synthesis and the nature of substrate are known to affect the property of deposited thin films. Aluminum (Al), Lead (Pb) and Zinc (Zn) were used as dopants for cuprous iodide (CuI) films at room temperature by SILAR method which affected the surface morphology, optical, structural and photoluminescence properties compared to undoped CuI thin film. The estimated energy band gap for the doped films varied from 1.90 to 2.30 eV.

L. A. Rochford et.al (2014), have used a prototypical copper iodide (CuI)/ planar phthalocyanine system to produce detailed surface and crystal structure information using

atomic force microscopy (AFM) and X-ray diffraction (XRD). The out-of-plane structure of the CuI layer was characterised and identified as the (111) plane of single crystal CuI. The dependence of surface morphology and grain size in the CuI (111) template layer upon substrate temperature was demonstrated. The formation of a thin film of iron phthalocyanine (FePc) on this model layer was characterised at multiple points during growth, changes in the surface morphology were observed, and the crystal structure of the final film was used to infer the molecular orientation therein.

2.1.3 Review of Manganese doped nanoparticles

Pairot Moontragoon et.al (2013), have prepared $Zn_{1-x}Mn_xO$ nanoparticles by PEG sol–gel method. Structure and morphologies of $Zn_{1-x}Mn_xO$ nanoparticles were investigated by using transmission electron microscope. Magnetic properties were measured by using a vibrating sample magnetometer (VSM). In calculation, electronic structure and magnetic properties for pure ZnO and $Zn_{1-x}Mn_xO$ have been investigated by means of the first principle calculations based on local density approximation (LDA) and LDA+U scheme, packaged in the ABINIT code.

L. Bruno Chandrasekar et.al (2015), have synthesised Mn-doped ZnS nanoparticles by simple and cost effective chemical precipitation method. This diluted magnetic semiconductor is characterized by various techniques such as energy dispersive X-ray analysis, scanning electron microscopy, X-ray diffraction, photoluminescence and UV–Vis spectroscopy. High purity of the sample is confirmed by energy dispersive X-ray analysis. Sub-micrometer nanocrystals are observed using scanning electron microscope. Hexagonal phase of the material is confirmed by X-ray diffraction studies, and the micro-structural properties such as grain size, strain, dislocation density and texture coefficient are examined.

Nanoparticles of Ce1-xMnxO2, (x=0.0, 0.01, and 0.05) have been synthesized by Shalendra Kumar et.al (2018) using co-precipitation method, and then characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM), near edge x-ray absorption fine structure (NEXAFS) spectroscopy and dc magnetization measurements. XRD results clearly showed that the all the samples have single phase nature and exclude the presence of any secondary phase. The average particle size calculated using XRD and TEM measurements found to decrease with increase in Mn doping.

Christine Barglik-Chory et.al (2003), have presented a novel colloidal route to photo luminescent CdS quantum dots and the doping of these nanoparticles with divalent manganese ions, resulting in emission caused by Mn^{2+} in addition to the band gap related emission of CdS. The semimagnetic semiconductor was synthesized using dithiol 1,2-bis(mercaptomethyl)benzene as stabilizer.

Williams, et.al (2013) have prepared Eu and Mn doped $NaMgF_3$ nanoparticles using a reverse micro-emulsion method. All nanoparticles show Mn^{2+}, Eu^{2+}, or Eu^{3+}photoluminescence (PL) and radio luminescence (RL) as well as PL from an unidentified defect that does not display RL. The Mn^{2+} sample contains PL emissions from distorted and undistorted Mn^{2+} sites but the RL is dominated by the undistorted Mn^{2+} site. The PL lifetime is lowest for the highest Eu concentration. This may be due to energy transfer from Eu^{3+} sites in the core to Eu^{3+} sites near the surface followed by non-radiative decay.

Kedarnath Gotluru et.al (2008), have synthesised $[Hg(TeCH_2CH_2{\cdot}NMe_2)_2]$ (**1**) as a yellow crystalline solid, which was characterized by elemental analysis, UV-vis, mass and NMR (^1H, ^{13}C, ^{125}Te, ^{199}Hg) spectroscopy. Thermolysis of **1** in hexadecylamine (HDA) at 90 °C in the absence and presence of $Mn(OAc)_2{\cdot}4H_2O$ gave undoped and Mn-doped HgTe

nanoparticles which were characterized by XRD, EDAX, TEM, EPR and magnetic measurements.

The structural, electrical and magnetoresistive properties of manganese doped cobalt ferrite nanoparticles have been investigated by M Z Ahsan, F A Khan (2018) through measurements of dc and ac magnetic properties. The samples were synthesized via standard solid state reaction route.

Casula et.al (2016), have developed a simple, one pot method to synthesize water-dispersible Mn doped iron oxide colloidal clusters constructed of nanoparticles arranged into secondary flower-like structures was developed. This method allows the successful incorporation and homogeneous distribution of Mn within the nanoparticle iron oxide clusters.

M. K. Bhide et.al (2008), have reported the synthesis of $Th_{1-x}Mn_xO_2$ (x = 0, 0.001, 0.002, 0.004 and 0.01 wt%) nanoparticles by the urea combustion method using thorium nitrate gel followed by heat treatment at a higher temperature (T). The obtained $Th_{1-x}Mn_xO_2$nanocrystals were characterized by X-ray diffraction (XRD), direct-current magnetization (M) measurements and electron paramagnetic resonance (EPR).

Ultrafine pure and Mn-doped SnO_2 nanoparticles (NPs) were synthesized via the microwave technique by Numan Salah et.al (2016). They were produced using tin chloride and hexamethylenetetramine at the molar ratio of 1:20. The concentrations of Mn in the SnO_2 matrix were in the range of 0.1–5 mol%. These nanomaterials were characterized using different techniques. SEM and TEM results show ultrafine NPs with sizes around 10 nm in both pure and Mn-doped samples. A single-phase rutile-type tetragonal structure was observed in pure and Mn-doped samples.

2.1.4 Review of Diluted magnetic semiconductors

B. Parveen et.al (2018), have synthesised Fe doped SnS nano-crystallites, with $X_{Fe} = 0.00–0.10$, by using cost-effective and simple co-precipitation method. X-ray diffraction (XRD) confirmed the orthorhombic single phase formation with nano-crystalline nature that is consistent with the surface structure revealed using SEM. NEXAFS spectroscopy has demonstrated that Fe retains +2 oxidation states. The ferromagnetism exhibited at 300 K also has revealed data storage device applications of the studied compounds.

Nanoparticles of ZnO and $Zn_{1-x}Mn_xO$ were synthesized by pulsed laser ablation in liquid medium (PLAL) by A. I. Savchuk et.al (2013). Metal zinc target was used for preparing of pure ZnO nanostructures and $Zn_{1-x}Mn_xO$ ceramic plates served for preparing of ternary nanoparticles. The Faraday rotation as a function of photon energy demonstrates behavior typical for diluted magnetic semiconductors (DMSs) in paramagnetic state.

Nanoparticles of ZnO and ZnO doped with transition metals (Mn, Co) were synthesized by laser ablation in liquid medium by Andriy I. Savchuk (2013). The Faraday rotation in ZnO:Mn nanoparticles gives evidence for paramagnetic behavior at room temperature.

Anup K. Ghosh et.al (2017), have investigated the structural, optical, magnetic, and electrical properties of sol–gel-derived $Ti_{1-x}Fe_xO_2 (0.00 \leq x \leq 0.05)$ nanoparticles. Magnetic measurements showed a weak ferromagnetism at room temperature in both the pristine and Fe-doped TiO_2 ($x = 0$, 0.02, and 0.05) nanoparticles. Temperature-dependent resistivity measurements showed the semiconducting nature of the samples and revealed that the thermally activated conduction (Arrhenius) mechanism is valid in the high-temperature region, whereas Mott variable range hopping (VRH) mechanism is valid in the low-temperature region.

S. Farjami Shayesteh and R. Nosrati (2015), have synthesized Ni-doped ZnO (Zn1−xNixO: x = 0.02, 0.04, 0.06, and 0.08) nanoparticles using a simple wet chemical precipitation method. The vibrating sample magnetometry measurement results of samples at room temperatures and annealed at 400 °C show a weak magnetic hysteresis loop that confirms the ferromagnetic properties of the samples. The origin of magnetic behavior in Ni-doped ZnO could be the presence of oxygen vacancies and exchange interaction between Ni ions. Also, the magnetic saturation of the samples increased with increasing Ni concentration in the range of 1.2 × 10−3 to 5.0 × 10−3 (emu/g).

With a view to study the structural, electronic, magnetic, and electrical properties of Zn0.9Ni0.1O diluted magnetic semiconductor nanoparticles, systematic investigation has been undertaken by P. Venugopal Reddy et.al (2011). Samples were prepared for the first time by hydrazine-assisted polyol method, and the powders were annealed at various temperatures in order to obtain the samples with different grain sizes. The magnetization studies were undertaken by VSM, MFM, and FMR techniques and confirmed the presence of clear room temperature ferromagnetism without any magnetic clusters.

Diluted magnetic CdS:Mn nanoparticles were synthesized by the aqueous solution method with different manganese (Mn2+) concentrations (x = 7–10 atom %) at room temperature in nitrogen atmosphere and capped with Thiogelycerol by S. Salimian and S. FarjamiShayesteh (2012). The room temperature ferromagnetic behavior of Mn-doped CdS nanoparticles is discussed by using hysteresis measurement results.

Muhammet (2017), has studied the magnetic properties of CoZnO materials according to size and shape effects using the Monte Carlo method and the Heisenberg Hamiltonian VAMPIRE software package. It was observed that size and shape control the magnetic disorder and temperature-dependent magnetization in Co-doped ZnO materials.

Tokeer Ahmad et.al (2013), have used a simple and modified solvothermal method using oxalate precursor, used to synthesize Cd1−xNixO (x = 0.047, 0.102, and 0.163) nanoparticles and their phase structure, morphology, optical and magnetic properties, have been investigated. The optical band gap of these solid solutions shows red shift to the undoped CdO. Ni-doped CdO nanoparticles exhibit co-existence of paramagnetism and ferromagnetism.

Cd/sub 1-x/Mn/sub x/S diluted magnetic semiconductor (DMS) nanoparticles of crystallite size ranging from 20 to 300 /splAring/ and x from 0 to 8.65 have been chemically synthesized by R.J. Bandaranayake et.al (1994) using aqueous solution precipitation. Magnetic properties of DMS particles have been measured with a SQUID magnetometer. A transition from a para-magnetic to a spin-glass state at a critical temperature has been observed.

M. Passacantando et.al (2006), have investigated the chemical, structural, and magnetic properties of MnGe alloys fabricated by ion implantation of Mn^+ at doses of 1×10^{16}, 2×10^{16}, and 4×1016at./cm^2 on Ge(100) single crystals at a substrate temperature of 300°C. Chemical maps obtained by electron energy loss spectroscopy reveal also the presence of manganese diluted in the host Ge matrix. The samples with higher doses are ferromagnetic with the Curie temperature approaching 270K. The sample implanted at the 1×10^{16}at./cm^2 dose exhibits ferromagnetic hysteresis only at 5K.

T. Ahmad et.al (2013), have reviewed the experimental developments and optical properties of oxide based DMSs, including the recent results on ZnO, CdO and In_2O_3 based systems. Optical properties of transition metal (TM)-doped ZnO, CdO and In_2O_3 dilute magnetic semiconductor nanoparticles show red shift in energy band gaps. Such types of phenomena are attributed to sp-d exchange interactions between band electrons and localized d-electrons of the substituted transition metal ions.

Li et.al (2016), have constructed Co-doped ZnO diluted magnetic semiconductor as a novel photoelectric beacon for photoelectrochemical (PEC) aptasensor of acetamiprid. The fabricated PEC sensing is based on the specific binding of acetamiprid and its aptamer, which induces the decrement of enhanced photocurrent produced by the electron donor of quercetin.

Jiangpeng Dong et.al (2018), have reported the capability of the diluted magnetic semiconductor Zn1-xMnxTe as potential THz emitters and sensors. In Zn1-xMnxTe crystals, a significantly enhanced THz response as high as 10.4%-18.9% (emitter) and 16.9-28.0% (sensor) is observed over intrinsic ZnTe. The magnetic, optical, and electrical properties of as-grown Zn1-xMnxTe crystals have also been evaluated.

Kataoka Takashi et.al (2010), have studied the electronic structure of Fe-doped ZnO nanoparticles, by X-ray photoemission spectroscopy (XPS), resonant photoemission spectroscopy (RPES), X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD). It is shown that the room temperature ferromagnetism in the Fe-doped ZnO nanoparticles is primarily originated from the antiferromagnetic coupling between unequal amounts of Fe3+ ions occupying two sets of non-equivalent positions in the region of the XMCD probing depth of approximately 2-3 nm.

2.1.5 Review of Magnesium doped nanoparticles

S.Suwanboon and P.Amornpitoksuk (2012) have synthesised Mg-doped ZnO nanoparticles by planetary ball milling at a speed of 400 rpm and milled for 20 h. The samples were characterized by XRD, SEM and UV-Vis spectrophotometer. The crystallite size of the samples increased and the lattice strain decreased with an increase of MgO loading. The increase in crystallite size of the samples as a function of MgO loading can be explained by the effect of Ostwald ripening.

Nanoparticles (NPs) of CdSe, a II-VI binary chalcogenide and Mg doped CdSe nanoparticles have been prepared by Microwave assisted method at room temperature by S. K. Choubey et.al (2018). CdSe nanoparticles have size-dependent photo-luminescence properties and promising applications in light emitting devices and anti-reflecting coating.

Yanfeng Gao et.al (2013), have reported the successful preparation of Mg-doped VO2 nanoparticles via hydrothermal synthesis. The metal–insulator transition temperature (Tc) decreased by approximately 2 K per at% Mg. The Tc decreased to 54 °C with 7.0 at% dopant. The composite foils made from Mg-doped VO2 particles displayed excellent visible transmittance (up to 54.2%) and solar modulation ability (up to 10.6%).

M. A. Behnajady et.al (2011), have prepared TiO2 and Mg-doped TiO2 nanoparticles with different dopant contents by sol-gel method. The prepared photocatalysts were characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET) and diffuse reflectance spectroscopy (DRS) techniques.

P.M. Md Gazzali et.al (2014), have synthesized nanoparticles of MgFe2O4 with average crystallite size of 8 nm employing non-aqueous combustion method. Structural properties of the nanoparticles are analyzed with the help of X-Ray Diffractometry (XRD), Scanning Electron Microscopy (SEM), Energy dispersive X-Ray analysis (EDX), Fourier Transform Infra-Red spectroscopy (FT-IR). X-Ray Diffraction pattern and FT-IR spectra reveal the formation of spinel structure of MgFe2O4 nanoparticles.

Jarnail Singh et.al (2018), have reported the synthesis, structural and optical studies of Mg doped nanoparticles of Chromium oxide (Cr2O3) prepared using co-precipitation method. These samples were characterized using powder X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), Raman spectroscopy and UV-Vis spectroscopy

techniques. The prepared Cr2O3 nanoparticles are spherical in shape, but they are transformed into platelets when doped with Mg.

Mirza Shirjeel Alam et.al (2016), have synthesized different concentrations of Mg-doped ZnO nanoparticles (NPs) by co-precipitation technique at 60°C. Finally, the sensing of UV light is tested by observing the response of nanoparticles by exposing them to UV light and measuring the resistance in presence and absence of UV light.

Yanna Chen et.al (2017), have investigated the lattice distortion and the electronic structure of MgxNi1−xO ($0 \leq x \leq 0.52$) thin films deposited on ultra smooth sapphire substrates using synchrotron x rays. Films with higher Mg content had lower values of Debye temperature and atomic order parameter.

H. Joy Prabu and I. Johnson (2015), have synthesized high-quality Mg doped ZnS nanoparticles by Greener cum chemical process with the assistance of polyvinyl pyrrolidone (PVP) with two different Mg concentrations. Doping of Mg metal in nanoparticles were found to be a good technique for tuning the band gap of ZnS nanoparticles. Simultaneously, Mg doping also inhibited the growth of crystallize size and it decreased from 33.2 nm to 18.3 nm with the increase in doping concentration from 0% to 5%. Band gap was found to rise from 3.12 eV to 3.38 eV and photoluminescence studies exposed that visible Photoluminescence (PL) emission was improved with doping concentration.

Monoclinic VO2(M) nanoparticles codoped with 1.5 at. % W and 2.9 at. % Mg were synthesized by Heesun Park et.al (2017) by the hydrothermal treatment and post-thermal transformation method of V2O5-H2C2O4-H2O with Na2WO4 and Mg(NO3)2. The reversible phase transition characteristics of the codoped VO2(M) nanoparticles and the composite film were investigated from DSC, resistivity and Vis-NIR transmittance measurements compared with the undoped and W doped VO2(M) samples. Mg-codoping into W-doped VO2(M)

nanoparticles synergistically enhanced the transition characteristics by increasing the sharpness of transition while the transition temperature (Tc) lowered by W-doping was maintained. The codoped composite film showed the prominently enhanced NIR switching efficiency compared to only W-doped VO2(M) film with a lowered Tc.

2.1.6 Review of Impedance studies of nanoparticles

Impedance spectroscopy employing slurry methodology was extended by Sasidhar Siddabattuni et.al (2015) to study the influence of various chemical groups on the nano TiO2 surface on the electrical resistivity and the dielectric permittivity of nanoparticles. In this regard, different organophosphate ligands with linear, aromatic and extended aromatic nature of organic groups were employed to remediate the surface effects of nano TiO2. It was observed that the type of chemical nature of surface engineered nanoparticles' surface played significant role in controlling the surface electrical resistivity of nanoparticles. Surface passivated nanoTiO2 yielded dielectric permittivity of about 70–80, respectively.

An impedimetric-based biosensor constructed using gold nanoparticles (AuNP) entrapped within titanium dioxide (TiO2) particles for hydrogen peroxide (H2O2) detection is developed by Nur Hamidah Abdul Halim et.al (2017). The matrix of the biosensor employed in the surface of TiO2, which was previously modified with an amine terminal group using 3-Aminopropyltriethoxysilane (APTS) at a low temperature to create a ready to immobilise surface for the biosensor application. Hemoglobin (Hb), which exhibits peroxidase-like activity, was used as the bioreceptor in the biosensor to detect H2O2 in solution.

Frequency and temperature dependent impedance, dielectric and conductivity studies of NdCr1-xFexO3 (x = 0, 0.2, 0.4, 0.6, 0.8, 1) perovskite ceramic nanoparticles in the frequency range 1Hz–1 MHz with various temperatures in the range RT-500 °C have been investigated by D. Suresh Babu et.al (2017). Impedance spectroscopy has been employed to

investigate the frequency, temperature and composition dependent impedance, dielectric and conductivity of the compound. The existence of grain and grain boundary effects has been observed. The frequency dependence of dielectric data has been used to investigate the conductive mechanism in the material.

Martina F Callaghan et.al (2010), have studied the impedance of gold nanoparticles. Bulk gold is well known to be highly conductive. If this were to remain the case on the nanoscale, it could be highly effective as a contrast agent for electrical impedance tomography, particularly when combined with tumour targeting.

B. Rajesh Kumar et.al (2012), have synthesized pure CdS and Ni doped CdS nanoparticles by chemical co-precipitation method using thiophenol as a capping agent. The frequency dependent dielectric dispersion of pure CdS and Ni doped CdS nanoparticles are investigated at room temperature in the frequency range of 100 Hz - 1 MHz by impedance spectroscopy. The dielectric properties and ac conductivity (σac) of the samples were measured as a function of frequency.

CdS and ZnS nanoparticles have been synthesized by Subhash B. Kondawar et.al (2010) using respective metal precursors and DMF as a stabilizing agent. The samples have been analysed by XRD, UV-VIS, fluorescence spectroscopy and TEM. Impedance analysis of the samples was carried out to reveal the variation of impedance with frequency at room temperature. These results shows the capacitive admittance associated with the nanoparticles and hence nanostructure CdS and ZnS can have potential applications in the electronics as nano-tuned devices in which resonant frequency can be adjusted by controlling the size and shape of the nanoparticles.

O. S. Doroshkevych et.al (2012), have developed an experimental spectroscopy method for investigating the electrical characteristics of concentrated nanopowder dispersed systems

based on compacted ZrO2. The technique is based on measurement of electrochemical impedance of the compacts. A possibility is shown for using the technique to study the processes of structure formation in nanopowder dispersed systems.

Lakshmi K. Singh et.al (2014), have studied the electrochemical properties of TiO2 nanoparticles using Impedance Spectroscopy (IS) to evaluate bulk and grain boundary effects which affects the transport properties of DSSCs.

R. Rajkumar and C. Vedhi (2018), have synthesized pure zinc oxide nanoparticles (ZnO) by a solution-free mechanochemical reaction using zinc acetate dihydrate and oxalic acid as the precursor. The corrosion inhibition efficiency of the nanoparticles were calculated for mild steel in 0.1M HCl and 3.5% NaCl solution using Electrochemical Impedance Spectroscopy (EIS) and Polarization (Tafel) studies.

Chien Chon Chen (2013), has studied the microstructure of the anodic tungsten oxide (WO3) and its use in an electrochromic (EC) glass device. When voltages between 100 V and 160 V were applied to tungsten film for 1 h under 0.4 wt. % NaF electrolyte, porous WO3 film was formed. The film, which had a large surface area, was used as electrochromic film for EC glass.

2.1.7 Review of theoretical studies of nanoparticles

J.A. Ascencio et.al (2001), have reported the experimental and theoretical studies of structural instabilities of gold nanoparticles supported on a carbon substrate using high-resolution transmission microscopy and molecular dynamics simulations. It is shown that particles undergo structural fluctuations in which a particle exhibits a change in orientation whilst maintaining the overall structure.

Huiyun Gao et.al (2011), have obtained a high quality surface-enhanced Raman scattering (SERS) spectrum of m-hydroxybenzoic acid (MHBA) on the surfaces of silver nano-

particles. In theoretical calculation, models of MHBA adsorbed on the surfaces of silver nano-particles were established and each of them corresponds to an experimental configuration. The Raman vibrational wavenumbers of these models using DFT-B3PW91 with lanl2dz were calculated; and it was compared with experimental spectrum.

Jens K. Norskov et.al (2005), have studied using Density Functional Theory the adsorption of molecules and the oxidation reaction of CO on gold clusters. Low-coordinated sites on the gold nanoparticles can adsorb small inorganic molecules such as O_2 and CO, and the presence of these sites is the key factor for the catalytic properties of supported gold nanoclusters.

Ye-Wan Ma et.al (2005), have studied the near-field spectral characteristics, images, and the optical parameters of silver nanoparticles using Green's tensor. The Lippmann–Schwinger integral equation is discretized, and numerically solved with complex-conjugate gradient method-fast Fourier transform algorithm. Simulation models include placing nanoparticles in either an infinitely homogeneous medium or on a substrate, and illuminated either directly with plane waves or through a glass substrate under total internal reflection.

MA Ye-Wan (2009), have studied the optical properties of silver nanoparticles such as extinction, absorption and scattering efficiencies based on Green's function theory. The numerical simulation results show that optical properties of silver nanoparticles are mainly dependent on their sizes and geometries; the localized plasmon resonance peak is red shifted when the dielectric constant of the particle's surrounding medium increases or when a substrate is presented.

Cristiana Di Valentin et.al (2017), have worked on a multistep/scale procedure to obtain global optimized minimum structures for chemically stable spherical titania nanoparticles of

increasing size, with diameter from 1.5 nm (~300 atoms) to 4.4 nm (~4000 atoms). They used first self-consistent-charge density functional tight-binding (SCC-DFTB) methodology to perform thermal annealing simulations to obtain globally optimized structures and then hybrid density functional theory (DFT) to refine them and to achieve high accuracy in the description of structural and electronic properties.

Gyun-Tack Bae and Christine M. Aikens (2015), have investigated the optical absorption properties of gold nanoparticles theoretically. A time-dependent density functional theory approach is employed to determine excitation energies for a set of three structural shapes: octahedra, truncated octahedra, and icosahedra (Aun, n = 6–85) in several charge states that correspond to electronic shell closings.

Surface enhanced Raman scattering (SERS) studies of N-benzoyl glycine (NBG) adsorbed on silver nanoparticles (AgNPs) was studied by A. Milton Franklin Benial et.al (2017) by experimental and density functional theory (DFT) approaches. Single crystals of NBG were prepared using slow evaporation method. The AgNPs were prepared and characterized. The DFT/ B3PW91 method with LanL2DZ basis set was used to optimize the molecular structure of NBG and NBG adsorbed on silver cluster. The calculated and observed vibrational frequencies were assigned on the basis of potential energy distribution calculation.

Puspendu Guha et.al (2017), have reported a simple single step growth of α-MoO_3 structures and energetically suitable site specific Ag nanoparticle (NP) decorated α-MoO_3 structures on varied substrates, having almost similar morphologies and oxygen vacancies. They elucidate the possible growth mechanisms in light of experimental findings and density functional theory (DFT) calculations. They experimentally established and verified

by DFT calculations that the MoO_3(010) surface is a weakly interacting and stable surface compared to other orientations.

Nanoparticles of Ag with different sizes and structures were obtained and studied by Álvaro de Jesús Ruíz-Baltazar et.al (2016). The results obtained by molecular simulation, cyclic voltammetry, and antibacterial effect were compared and discussed in this work.

2.1 Scope of the present work

Nanoparticles have one dimension that measures 100 nanometers or less. The properties of many conventional materials change when formed from nanoparticles. This is typically because nanoparticles have a greater surface area per weight than larger particles which causes them to be more reactive to some other molecules.

Copper iodide (CuI), a p-type direct bandgap semiconductor, has attracted the research community for many years because of its wide bandgap, negative spin-orbit splitting and high ionicity, an unusually large temperature dependency, anomalous diamagnetism behavior, , new high pressure phase etc. It has potential applications in superionic conductor, solid-state solar cells, catalysis for synthesis of organic compounds and others. Nano size CuI is being pursued with great interest because of several possible technical applications in catalysis, drug delivery systems, separation techniques, photonics as well as piezoelectric and other dielectric devices.

Most recently, the field of diluted magnetic semiconductors (DMSs) has gained the attraction of the researchers due to their exclusive properties and their increasing demand in the areas of device physics such as optoelectronic and spintronics. The spin-dependent magnetic phenomena can be manipulated in the low-dimensional tailored magnetic DMSs thin films for various spin-based devices to unprecedented capabilities. The main challenge in the practical applications of the DMS materials is the attainment of ferromagnetism (FM) above room temperature (RT) to be compatible with junction temperatures.

From the literature review it is observed that the reports related to CuI nanoparticles and CuI thin films and their change in optical, magnetic and electrochemical properties on doping are limited.

Hence we are interested to synthesise CuI nanoparticles, CuI thin films, Magnesium doped CuI nanoparticles and Mn doped CuI thin films and characterise them using various spectroscopic techniques. Also the magnetic and impedance studies of the Manganese doped thin films and Magnesium doped CuI nanoparticles respectively, are to be investigated. Also we have planned to carry out the theoretical studies on CuI nanoparticles.

The scope of the present investigation is as follows:

1. To synthesise copper iodide (CuI) nanoparticles by conventional precipitation method.
    - To characterise the synthesised CuI nanoparticles using XRD, FT-IR, UV-DRS, photoluminescence and SEM-EDAX techniques.
    - To study the effect of annealing temperatures (100°C, 200°C, 300°C and 400°C) on the synthesised CuI nanoparticles.
2. To synthesise copper iodide thin films and manganese doped copper iodide thin films by SILAR method.
    - To characterise the synthesised CuI thin films using XRD, UV-DRS, photoluminescence and AFM techniques.
    - To characterise the synthesised Manganese doped CuI thin films using XRD, UV-DRS, photoluminescence and AFM techniques.
    - To study the magnetic behaviour of the synthesised CuI and Manganese doped thin films using vibrating sample magnetometer.
3. To synthesise copper iodide nanoparticles and magnesium doped copper iodide nanoparticles by conventional precipitation method.

- To characterise the synthesised CuI nanoparticles using XRD, FT-IR and UV-DRS.
- To characterise the synthesised magnesium doped CuI nanoparticles using XRD, FT-IR, UV-DRS.
- To carry out the electrochemical impedance analysis of the synthesised CuI nanoparticles and magnesium doped nanoparticles.

4. To study the structural, optical and electronic properties of copper iodide nanoparticles with the help of Density Functional Theory using Wien2k code employing the following potential functions.

- TB-mBJ
- GGA