“SYNTHESIS AND CHARACTERISATION OF NANOCRYSTALLINE SEMICONDUCTING CHALCOGENIDES BY POLYMER-INORGANIC SOLID-STATE REACTION”

A MINOR RESEARCH PROJECT PROPOSAL FOR FINANCIAL ASSISTANCE

COMPLETION REPORT
AUGUST 2015

SUBMITTED TO

UNIVERSITY GRANTS COMMISSION

NEW DELHI

BY

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UNIVERSITY GRANTS COMMISSION
COMPLETION REPORT
Reference: UGC (WRO) sanction letter no. F.47-297/12(WRO) dt.05.02.2013

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ANNEXURE-I

Actual submitted proposal

PROJECT TITLE

SYNTHESIS AND CHARACTERISATION OF NANOCRYSTALLINE SEMICONDUCTING CHALCOGENIDES BY POLYMER-INORGANIC SOLID-STATE REACTION

INTODUCTION

Nanoscience deals with small structures or small-sized materials. The unit of nanometer derives its prefix *nano* from a Greek word meaning extremely small. A nanometer is one billionth of meter, or 10^{-9} m. One nanometer is roughly the length occupied by five silicon or ten hydrogen atoms aligned in a line.

In general, nanotechnology can be understood as technology designed for fabrication and application of nanostructures and nanomaterials. Nanostrutured materials are those materials having at least one dimension falling in nanometer scale, and they include nanoparticles, nanorods, nanowires, thin films etc.

The nanoscale science and technology has introduced new trends that involve the ability to synthesize, characterize and manipulate artificial structures, whose features are controlled at the nano level. It encompasses areas of research as diverse as engineering, physics, chemistry, material science, and molecular biology. The research in this area has been set off by the recent availability of revolutionary instruments and approaches that allow the investigation of material properties with resolution close to atomic level.

When the particles are altered from centimeter size to nanometer size, the surface area and surface energy increase several orders of magnitude. Due to vast surface area, all nanostructured materials possess a huge surface energy and thus are thermodynamically unstable or metastable. One of the great challenges in fabrication and processing of nanomaterials is to overcome the surface energy and to prevent the nanostructure or nanomaterials from growing in size, driven by the reduction of overall surface energy. For example, liquid and amorphous solids, they have isotropic microstructure and thus isotropic surface energy. For such type of materials, reduction of the overall surface area is the way to reduce the overall surface energy which produces zero dimensional (O-D), nanostructure. However, in crystalline solid, different crystal faces possess different energy which may produce one dimensional (1-D) and two dimensional (2-D) nanomaterials.

The intentionally produced Nanomaterials are classified into four main types: as carbon based materials, metal based materials, dendrimers and composites.

Several methods have been accomplished for the synthesis of different types of nanoparticles using mainly two approaches i.e. top-down and bottom-up. Attrition or milling is the typical top-down method including repeated quenching and lithography in making nanoparticles. The preparation of nanomaterials in the form of colloidal dispersion is a good example of bottom-up approach in the synthesis of nanoparticles.

The first way top-down is to start with a bulk material and then break it into smaller pieces using mechanical, chemical form of energy. An opposite strategy i. e. bottom-up, is to synthesize the material from atomic or molecular species via chemical reactions, allowing for the precursor particles to grow in size. Both strategies can be done in either gas, liquid, supercritical fluids, solid states, or in vacuum.

In the context of the chemical design of inorganic materials, the challenge is to synthesize nanostructure in thermally modified polymer matrix Polymer as stabilizing matrices or capping agents help to provide good mechanical and optical properties as well as confer high kinetic stability on nanometer- sized particles.

Keeping this in mind, we here in propose to carry out research on the synthesis and characterization of nanoparticles such as Nickel, Nickel oxide, Nickel sulphide, Manganese, Manganese oxide, Manganese sulphide etc. produced by novel polymer- inorganic solid state reactions. Polymer will be used as a matrix and an inorganic salt will be used as a cation precursor to synthesize the desired nanostrucrure in thermally modified polymer matrix. We would also explore the feasibility of these nanomaterials for photovoltaic devices, solar cells and sensor applications.

ORIGIN OF RESEARCH PROBLEM:

Synthesis and characterization of nanocrystalline semiconducting chalcogenides.

INTERDISCIPLINARY RELEVANCE:

Collaboration with Physics departments – Characterisation and data interpretation.

Collaboration with Electronics departments – Characterisation and data interpretation.

INDIAN STATUS :

In India many amazing surface dominated properties, which arise as a result of quantum confinement, are of both academic and technological interest to researchers. In the past few years, there is a massive influx of literature reports dealing with various approaches focusing on the synthesis of semiconductor nanoparticles. Conventionally, ionic reactions in liquids, gas liquid precipitation, and solid-state reactions have been utilized to prepare Q-semiconductors. Also solvo-thermal methods, low temperature synthesis, liquid ammonia synthesis, thermolysis have been reported. Low molecular weight thiols, polyphosphate, polymers dendrimers, block co-polymers have been intentionally added as stabilizers for controlling/ arresting the agglomeration propensity of semiconductor nanoparticles. Polymers, in particular, apart from their stabilizing action provide good mechanical and optical properties, as well as confer high kinetic stability on nanometer sized semiconductor particles. Quite curiously, the scope of using polymer as a reactant in the synthesis of nano semiconductors is hitherto unattempted! In this work, we propose to unveil simple solid-solid reactions in which polymer serves dual purpose namely a reactant for anion source and a capping/stabilizing agent.

We herein propose to carry out research on the synthesis and characterization of chalcogenides semiconductor nanoparticles by the novel inorganic-polymer solid-solid reaction route. Polymer will be used as chalcogenides precursor and an inorganic salt will be used as a cation precursor to synthesize the desired

INTERNATIONAL STATUS:

Nanotechnology applications are a reality today. American car manufacturers have been using nanotubes to improve the safety of fuel-lines in passenger vehicles for over a decade, and the electronics industry has been relying on nanotubes in its packaging material to better protect goods and to aid the removal of any electrical charges before they can build to disruptive levels. Japan, Korea, Taiwan, and European countries including Scotland and the Netherlands have also played influential roles in the development of nanotechnology capabilities - and the technology continues to be of world-wide interest.

The potential for more broad-based nanotechnology applications will come from a better understanding of how particles operate on a nanoscale and how biological and non-biological particles can be integrated - research and development continues in these fields and many others. There is still a way to go before we fully understand the workings and potential applications of the assembly of atoms and how to make these processes scalable, profitable and standardised (and therefore able to produce predictable and consistent outputs).

Around US$2 billion is being invested annually in nanotechnology developments around the world, with nearly 40% of this in the USA. Japan is a major contributor, as are the European Governments and major industrial economies such as Singapore, Taiwan, and China.

SIGNIFICANCE OF STUDY :

The new trend in the synthesis of nanoparticles is to find the simple technique for the synthesis of nanomaterials and to development of facile single step in-situ generation of metal/metal sulphide nanoparticles over a range of sizes (with good monodispersity) and chemical composition. Hence, our approach is directed towards the development of simple experimental technique for the synthesis of nanomaterials.

This is the salient feature of the proposed work, in which we strongly emphasised on the simple and single step for the fabrication of Ni_2S nanostructures in hetero-matrices by solid-solid reaction. In this methodology, the intentionally chosen thermoplastic polymer polyphenelene sulphide (PPS) served the dual purpose, namely as a sulphur source and as a stabilizing agent. This is one of the most attractive facile methodologies for the direct synthesis of Ni_2S nano-powder. The process reported here are cheaper, simple and useful for large-scale production.

Therefore, the present work is mainly focused on the synthesis and characterization of nanocrystalline Ni_2S which are often used as a photo sensitizer in photography process, principal element in thermo power cells and also in photoconducting cells, IR detectors, solar selective coatings, photovoltaic cells etc. Besides, they exhibit good chemical stability and excellent optical limiting properties. With this simple and “easy-to-cook” recipe, various types of nanomaterials with different reaction parameters can be prepared.

OBJECTIVES :

- To synthesize nanoparticles of the different metals as well as metal oxides and metal sulphides (viz , Nickel, Nickel sulphide, and Nickel oxide and also of different metals such as Zinc, Manganese, Copper, Iron etc.) by Polymer-inorganic Solid State Reactions.
- To study the physical and optical properties of synthesized nanomaterials.
- Applications in all kind of sectors and products, e.g. electronic, optical etc.

METHODOLOGY :

Synthesis of metal, metal oxide, metal sulphide nanoparticles.

To demonstrate the feasibility of the in-situ generation of metal, metal oxide,metal sulphide nanoparticles in polymer matrix via proposed solid state route, we propose a plan to attempt the reactions involving precursor metal salts like metal acetate, nitrate, chloride,carbonate and engineering Polymer The synthesized product will be subjected to natural cooling to room temperature. The powder thus prepared will be used to carry out physico-chemical characterizations and application oriented studies. We propose to carry out synthesis of nanostructures of Zinc, Zinc Oxide, Nickel, Nickel sulphide, Nickel oxide, Manganese, Manganese oxide and Manganese sulphide etc., by polymer–inorganic solid state reaction and study the structure, morphology and allied properties of the synthesized nanoparticles. The feasibility of these nanomaterials for applications in photovoltaic devices, solar cells and sensors will be studied.

YEAR WISE PLAN OF WORK :

First Year :

a) Literature survey
b) Establishment of the solid-state reaction technique
c) Identification of process parameters responsible for the synthesis of nanoscale materials
d) Synthesis of nanoscale materials and optimization of process parameters

Second Year :

a) Characterization of nanoscale materials by various techniques.
b) Establishment of relation between process parameters and resulting nanoscale materials properties.
c) Preparation of final report
d) Dissertation writing.

(a) Amount sanctioned

	Item	Expenditure
i)	Field Work and Travel	10,000.00
ii)	Chemicals and glassware	40,000.00
iii)	Contingency	10,000.00
iv)	Equipments	30,000.00
iv)	Books and Journals	10,000.00
	Total	1,00,000.00

ANNEXURE-II
WORK DONE:

YEAR WISE PLAN OF WORK:

First Year:

- Literature survey
- Establishment of the solid-state reaction technique
- Identification of process parameters responsible for the synthesis of nanoscale materials
- Synthesis of nanoscale materials and optimization of process parameters

Second Year :

- Characterization of nanoscale materials by various techniques.
- Establishment of relation between process parameters and resulting nanoscale materials properties.
- Preparation of final report
- Dissertation writing

1.Introduction:

Recently, much attention has been focused on the development of polymer/inorganic nanohybrid materials. Inorganic semiconductors like ZnO, TiO_2, MnO_2, and ZrO_2 have been widely examined as hybrids with polymers having synergetic or complementary properties and activities for the fabrication of a array of devices. Among these semiconductors, ZnO has shows potential applications in electrical engineering, catalysis, ultraviolet absorption, photodegradation of microorganisms, and optical and optoelectronic devices. Even if ZnO demonstrate many advantages, there are still numerous disadvantages, for example the lack of visible light response, low quantum yield, and lower photocatalytic activity. Furthermore, it is significant to shift the photo activation region of ZnO particles toward visible wavelengths.Prior studies verified that conducting polymers incorporated with ZnO could exhibit rational catalytic activity under light illumination, and the delocalized conjugated structures of conductive polymers have been verified to arouse a rapid photo induced charge separation and decrease the charge recombination rate in electron transfer processes. Nonetheless, ZnO is an amphoteric oxide, and it can react with acid or base to form a water-soluble salt. Consequently, a flourishing inclusion of ZnO into a conducting polymer matrix is the major research topic. Currently, there are numerous reports on the preparation methods of conducting polymer/ZnO composites, and the methods are mainly electrochemical polymerization and mechanical mixing. On the other hand to the finest of our knowledge, synthesis of nanocomposite/1-D nanostructure using polymer as inherent chalcogen source has not been sincerely attempted. In this framework, vide this communication, we projected into the synthesis of 1-D ZnO nanostructure within polyphenelene sulphide matrix using superficial and novel solid-state reaction method with the intension to learn the effect of molar ratio (1:1) on the reactants- zinc nitrate and PPS. Here PPS acts as stabilizer as well as a chalcogen precursor. In addition, PPS with its exceptional mechanical and chemical properties can be processed in any desired form, which could be important aspects from the perspective of nanocomposite based fabrication.

2.Material and methods: Polyphenelene Sulphide(PPS) with number average molecular weight of 10,000, zinc nitrate andacetone were obtained from Aldrich (99% purity)and were used as received. Zinc nitrate salt were used as Zn source, in both the sets of experiments. The melting temperature (Tm) of PPS is 285 ºC and its thermal decomposition starts at ~ 450 ºC. Therefore, the reaction temperature 285 ºC was chosen for the synthesis of ZnO in PPS matrix as at the melting temperature, sulphur will be loosely bound and some loosely bound sulphur may react with zinc to form ZnO.In-situ synthesis of zinc oxide in polymer matrix via proposed solid state root was carried out with reactants (zinc nitrate :PPS) using 1:1 ratio. For such reactions , the two reactants were admixed in stated molar ratio in a beaker and stirred for half an hour and then this mixture was transferred in an agate pestle- mortar using acetone. The resultant mixture, after drying at room temperature was subjected to heating at 285 ºC(melting temperature of PPS) in an alumina crucible for 5 hours under an ambient atmosphere. Subsequently, it was naturally cooled down to room temperature. The obtained products with 1:1 molar ratio were of white coloured fine powder sample.

3.Theory: The choice of the polymers is usually guided mainly by their mechanical, thermal, electrical, optical and magnetic behaviors. The polymer in many cases can also allow easier shaping and better processing of the nanomaterial. Hence we have selected such a polymer which play important role of stabilization. The inorganic salt zinc nitrate provide the metal which get into the polymer matrix . This method suggest superficial generation of ZnO merely heating the precursors at constant temperature of PPS. Also product which we obtained is in sufficient amount as we allowed for reaction. Therefore this method is cost effective.

4.Results and Discussion: The X-Ray powder Diffraction pattern of the synthesized sample were recorded with Rigaku Miniflex X-ray Diffractometer using Ni filtered CuKα radiation. The external morphology and particle size of the sample were characterized by Scanning Electron Microscopy (SEM: Hitachi S 4800). For SEM analysis, the sample were prepared by (dispersing the obtained powder in methanol followed by ultrasonication treatment for 10 min) mounting a drop of nanoparticle solution on an aluminium stub and allow it dry in air. The XRD pattern of the synthesized ZnO nanoparticles is shown in figure-1, corresponding to 1:1 molar ratio of $ZnNO_3$ with PPS heated at 285 ºC with constant reactant time of five hours. As shown in the fig 1., the peaks at 2θ=31.766,34.463,36.259, .545, 56.600, 62.841, 66.370, 67.990, 69.141,72.527,76.974 can be readily indexed as Hexagonal ZnO structure in the agreement with the reported JCPDS Card No. 36-1451. The strong and broadened peak at 2θ = 36.259indicates that the material has good crystallinity and small size. Also peak at 101 is much stronger than the other diffraction peaks. The key particle size has been calculated from FWHM values of strongest peak for 1:1molar ratio is in the range of 27nm for sample corresponding to zinc nitrate with PPS. The FESEM photomicrographs of sample product corresponding to 1:1 molar ratio are presented in Fig 2(a,b). The hexagonal structure like morphological feature (of size 5-20µm) are observed in Fig 2(a). Such features appeared to be characteristics of ZnO nanoparticles indexed by X-ray diffraction data. Also flower like morphology appeared in Fig 2(b) photomicrogaphs which can be attributed with ZnO nanoparticles in polymer matrix. The chunk like morphologcal features in fig 2(b) appeared to be characteristics of PPS.

5.**Conclusions**: We have demonstrated superficial solid-state method for the synthesis of ZnO nanoparticle in polymer matrix using metal salt $ZnNO_3$ with PPS as precursors. The strong diffraction peaks are observed, confirming the formation of ZnO nanoparticles which arestrongly supported by FESEM images. Such ZnO nanoparticles may be useful in electrical engineering, catalysis, ultraviolet absorption.

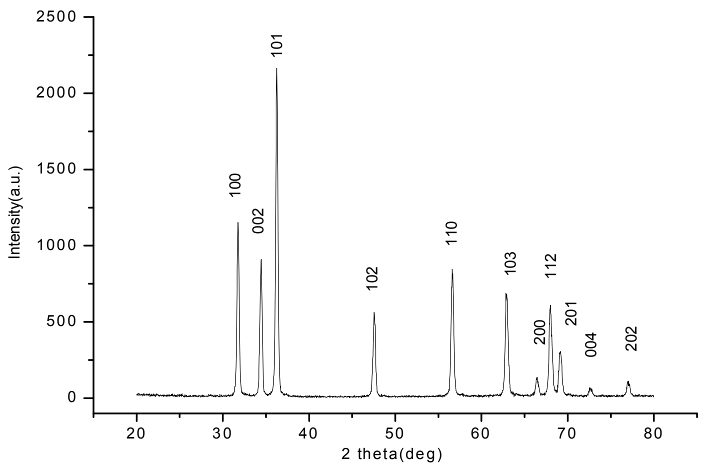

Fig. 1. X-ray diffractogram correspond to heated admixture of PPS and zinc nitrate in molar ratio of 1:1.

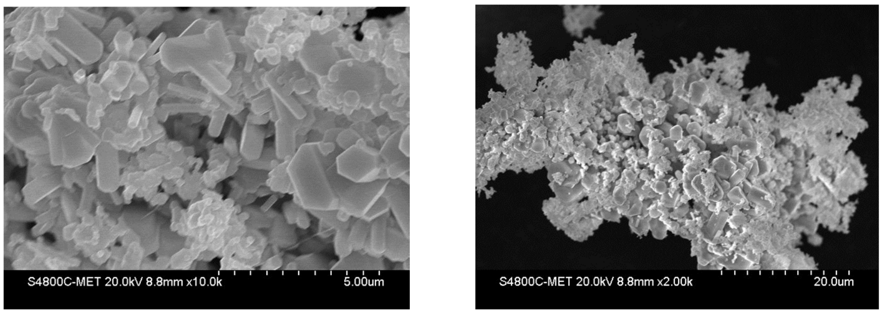

Fig. 2. FESEM images (a) and (b) correspond to heated admixture of PPS and zinc nitrate in molar ratio of 1:1

Acknowledgements

Generous funding by University Grant Commission (UGC) under minor research project is gratefully acknowledged. We are indebted to Dr. U.P. Mulik, Dr. Dinesh Amalnerkar(Executive Director), Dr. Parag Adhyapak, Manish Shinde of C-MET. We also wishes to acknowledge constant encouragement received from the Principal and Management Committee of MES Society's Abasaheb Garware College, Pune.

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Outcome of the project

Annexure-III

1. **Sujata Kasabe,** Tanuja Gumaste, Parag Adhypak, Uttam Mulik, Dinesh Amalnerkar**(2014)**. A superficial solid-state heating method for the synthesis of zinc-oxide nanoparticles in polymer matrix. ***Proceedings*** Nanocon 014 3rd International conference **p.73.** Bharati Vidyapeeth Deemed University, Pune.
2. **Sujata Kasabe,** Manish Shinde, Parag Adhypak, Uttam Mulik, Dinesh Amalnerkar**(2015)**. Synthesis of zinc-oxide nanoparticles in polymer matrix. ***Proceedings National conference. p.73*** Chemistry of Chalcogens. DIAT, Pune.
3. **Sujata Kasabe**, Parag Adhyapak, Uttam Mulik, Dinesh Amalnerkar, Chetan Bhongale **(2015)**. " A Superficial Solid-State Heating Method for the Synthesis of Zinc- Oxide Nanoparticles in Polymer Matrix" **IJITE**, **Vol. 09, No.1, (Impact factor 3.570) .**

Name and Signature,

Principal Investigator,

UGC (WRO) sanction letter no. F.47-297/12(WRO) dt.05.02.2013

Dr. R. C. Chikate — **Dr. Shrikant Gupta**

Head, Dept. of Chemistry — **Principal**