INDO SWISS JOINT RESEARCH PROGRAMME (ISJRP)

JOINT UTILISATION OF ADVANCED FACILITIES

EXCHANGE GRANT REPORT

Grant No.: JUAF17

Part 1 - General Information

Project Title: Semiconductor nanowires and nanocomposites for solar cell applications and their photonic characterization

Keywords: Photonics, nanowires, semiconductors, solar energy

Start date/ Duration: August 1st, 2010 (2 months)

Part 2 - Exchange Participant(s) Details

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Part 3 - Scientific & Technical Information

3.1 Purpose of visit

(Briefly describe the purpose and goals of this exchange.)
The optimal utilization of the solar light impinging on solar cells depends not only on the proper choice of materials and their stoichiometric mix, but also on their meso- and nanostructure and architecture. In addition to proper alignment of energy bands and match of the band gap with the solar spectrum, the light scatter properties should be adjusted so that no light is scattered away. The concept of “photonic materials”, materials with an architecture the functionality of which scales with the wave lengths of visible light, is in this respect very interesting and has not yet taken centre stage in solar cell design. Empa’s Laboratory for High Performance Ceramics (LHPC) has recently started activities in solar cell materials science and technology. The experience of Fellow Dr. S. Ani-Joseph in photonic materials and characterization is of high interest for LHPC. Both partners have already published independently work relevant for the project recently [1,2].
The purpose of the visit is that 1) nanostructured materials developed at CUSAT are measured with electron microscopy, x-ray diffraction and photoelectrochemical methods at Empa in Switzerland, and that 2) nanostructured materials developed at Empa are measured with linear and non-linear optical spectroscopy methods at CUSAT, and thus a mutual sensitization of staff and students at the host and fellow institutes for the different fields of expertise and their complementary is gained.

3.2 Short description of work carried out during the visit

(Please describe the technologies acquired and the experiments/activities performed during the course of the exchange.)
The work was organized as follows:
1) Dr. Ani-Joseph stayed and worked in August and September 2010 at Empa and participated in measurements of samples she brought from CUSAT. This included CdS and ZnO based nano-sized systems, which were subject to electron microscopy at the Center for Electron microscopy, x-ray diffraction at the Laboratory for Catalysis and Solid State Chemistry, and photo-electrochemical experiments at Empa LHPC. IPCE measurements were conducted at EPFL Lausanne in the Laboratory for Photonics and Interfaces. Spin-coating experiments were carried out at the Laboratory for Functional Polymers.
In return,
2) PhD student Debajeet K. Bora stayed in November 2010 at CUSAT in order to have his Fe2O3 based photoanodes investigated with optical spectroscopy methods.

Experiment 1:
Study of linear and non-linear optical properties of hematite nanoflowers ((a) 6 thin films of hematite nanoflower deposited on 1.5 mm thick conducting glass substrate, (b) 6 colloidal nanoflower suspensions prepared with double distilled water) grown at different time with basic photonics methods, i.e. Absorbance, Transmittance, Reflectance spectroscopy and Non Linear Susceptibility measurement using the Z–scan method.
Experiment 2:
Study of linear optical properties, i.e. absorbance, transmittance, and reflectance of nanostructured, hematite-zinc oxide binary photoelectrodes ((a) 4 films of ZnO on hematite grown hydrothermally and (b) 4 films of hematite on ZnO).

Experiment 3:
Study of linear optical properties with absorbance, transmittance and reflectance of hematite–photosynthetic protein conjugates, i.e.5 thin films of hematite / photosynthetic protein based system.

Photo: Front – ISJRP Fellow Dr. S. ANI-JOSEPH; Back from left to right: Dr. Rolf ERNI, Head of Empa Electron Microscopy Center; Dr. Artur BRAUN ISJRP-PI, M.Sc. Debajeet. K. BORA, PhD student at Empa and University of Basel.
3.3 Outcomes

(Please describe the main results obtained during the course of the exchange.)

ZnO Nanostructures

ZnO (large band gap energy of 3.3 eV) nanoparticle films were grown based on a recepture containing KOH, ethanol and zinc acetate, with particle size of several ten nanometers, but no particular architecture, see Figure below.

Figure:

Tuning of the process parameters allowed us finally to obtain hexagonal nanorods, see Figure below.

Figure: SEM of ZnO nanorods prepared by Visiting Fellow Dr. Ani-Joseph and Empa PhD student D.K. Bora.
Figure: Incident photon to current efficiency (IPCE) of Si doped hematite, nanoflower hematite, and ZnO deposited as ZnO nanoparticles and ZnO nanorods on hematite. The ZnO functionalization of hematite does not yield a higher IPCE. There is also no increase in photocurrent upon functionalization of hematite with ZnO.

CdS Nanostructures
Figure: CdS nanoparticles of 2.5 nm diameter (!) synthesized by the Visiting Fellow’s Lab at CUSAT. For comparison with CdS nanoparticles from literature see Figure below.

_D. Philip / Physica E 41 (2009) 1727–1731_

Fig. 6. TEM images of CdS colloidal: (a) low magnification; (b) high magnification and (c) SAED pattern.

Figure: Reference images of CdS from literature, Physica E 41 (2009) 1727.
Ag:TiO2 Nanostructures

TiO2 catalyst particles were functionalized by silver metal nanodots. One question is whether the deposited silver metal dots are in reduced or oxidized state after processing. It is likely that they oxidize in the ambient but it is not sure whether they are readily oxidized in the solution they are contained in. Therefore X-ray diffraction was performed on the materials using BN capillaries which contained the nanoparticles in solution.
Figure: SEM micrograph of Ag:TiO2 – silver nanoparticles on TiO2 photocatalyst nanoparticles.

SEM
3.4 Future collaboration with host institution

(Please provide information on future collaboration opportunities and follow-up activities.)

3.5 Various comments

(E.g., what worked well, what didn't work well, suggestions and improvement ideas, ...)

Nanoparticles for optical applications were synthesized by various methods and subjected to morphological, structural and electrochemical characterization at EMPA prior to visit of the Indian scientist. The systems of choice were Fe$_2$O$_3$ hematite and ZnO.

The Indian (ISP) and Swiss partners (EMPA LHPC) aimed at collaborating on materials and architectures for solar energy conversion and lighting applications, employing self organized growth mechanisms. The main objective of this Indo-Swiss project was exploration and development of strategies for the synthesis of semiconductor architectures with relevance and potential application to solar cell electrodes and similar photonic applications. The materials that were intended to be explored were Fe, Ti, Zn and Cd based oxides and sulfides or selenides. Geometries and structures include nanowires, be they free standing or fixed on supports, and nanocomposites such as nanoparticles. To exploit plasmon effects, the studies were planned to be functionalized with metal particles such as Ag, Au, or Pt.

The research group at the international school of photonics synthesized nanoparticles of CdS, ZnS, TiO$_2$ and nanocomposites of Ag:TiO$_2$, nanowires of ZnO and nanorods of silver for this purpose and were taken to EMPA for further studies. The optical (linear and nonlinear) and photothermal studies of most of these systems were already completed at ISP prior to visit at EMPA while some other photonic characterizations are still going on.

Laser irradiation was employed at ISP for the synthesis of Ag: TiO$_2$ and nanoparticles form by laser induced chemical reaction. Different irradiation times were used for optimization of nanoparticle formation. Initial structural characterizations were done at CUSAT, India and later at EMPA XRD, SEM and TEM were done to get better insight into the crystallographic properties, relative percentage of silver and TiO$_2$ in the composite, particle size, morphology of the nanocomposite systems etc which helps in standardizing the synthesize technique. The xrd done in powder form and I the liquid forms of the sample throw light on whether the crystalline properties change when the sample is dried.
to powder. Most of the photonic experiments to measure the efficiency of the material as laser media are done in liquid form. The nonlinear optical properties and heat diffusion efficiency of these structures shall be communicated to a suitable photonics journal immediately. Later, the hematite nanostructures from EMPA shall be sensitized using these composites and modification in optical properties shall be investigated during the visit of the PhD student from EMPA to ISP CUSAT during the end of this year.

ZnO nanowires from ISP were imaged using SEM at the electron microscopy center, EMPA which did not show expected features; presumably due to short shelf life of the nanostructures. Submicrorods of ZnO were resynthesized at EMPA and its TEM, SEM, HRTEM, SAED etc were carried out. The hematite films were sensitized using these rods and their IPCE (incident photon to current conversion efficiency) was measured at Gratzel, EPFL. Eventhough the current conversion efficiency of the hematite films did not show an enhancement in the presence of ZnO, the results show promising features in the IPCE curve pointing to ZnO micro rods’ possible application as laser ring resonator. These studies are going on at ISP at present.

CdS, TiO2 and ZnS nanoparticles were imaged using TEM and their XRD were done. SEM was also done on several sets of these samples after drying few drops on a glass plate. Some samples of TiO2 showed tendencies to self organize. The size of these quantum dots fall within the strong confinement regime (less than 5 nm) as evidenced from optical exciton formation and fluorescence studies carried out previously at ISP. This information was substantiated by the TEM and XRD results at EMPA. Attempts were made to spin coat the quantum dots on ITO glass and measure the photocurrent efficiency after depositing gold electrodes. To verify the continuity of the coated films AFM images were taken.

As the second phase of this project, bandgap measurements of hematite nanoflower films sensitised with several types of quantum dots shall be carried out at ISP during Nov-Dec 2010. The bandgap renormalization of nanoparticles can be found from the shift of the PL peak energy after carrying out the laser excited fluorescence studies.

Nanoparticles of ZnO deposited on ITO glass shows great stability after annealing at high temperatures. The optical properties of these structures shall be investigated and later the nonlinear optical characteristics of solutions of hematite nanostructures and ZnO films shall be carried out at ISP to complete the project.

3.6 Projected publications/articles resulting or to result from the exchange

(if applicable)


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