



Synopsis Report: Mr. Saptak Rarotra

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Abstract

In the present thesis, we explore a number of simple and cost-effective pathways to develop micro and nano devices useful for energy harvesting applications. The proof-of-concept prototypes developed can be employed to tap upon the clean and renewable resources of energy and convert them into other usable forms such as the electrical or chemical energy. In this regard, while microreactors are employed as advanced flow reactors for the conversion of solar energy into the chemical one, the mesoscale conducting polymer droplets are employed to convert solar to electrical energy. The content of the thesis is divided into four research objectives alongside an overall introduction in the beginning and important conclusions summarized at the end. The **Chapter 2** of the thesis deals with microfluidic electrolyzers for production and separation of hydrogen from sea water using naturally abundant solar energy. In the process, we also demonstrate the development of a potable, energetically self-reliant, environmentally-benign, and eco-friendly prototype for this purpose. Following this, the **Chapter 3**, of the thesis deals with graphite and reduced graphene oxide coated paper based microelectrolyzer for the continuous production and separation of pure hydrogen and/or oxygen from sea water with the help of solar energy. In the **Chapter 4**, we demonstrate a microfluidic reactor for continuous production of organics from carbon dioxide and sea water in which the energy required for the reactions has been obtained from the electrical energy produced by a solar cell. In the process, we demonstrate a potable, energetically self-reliant and eco-friendly device converting carbon dioxide into organic fuels. The **Chapter 5** shows the details of the spin-dewetted conducting polymer droplets as micro/nano solar energy harvesters. Finally, we summarize the thesis in the **Chapter 6** with the important conclusions drawn from the research objectives and the future scopes associated with the extension of these works.

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Chapter 1: Introduction

In the recent times, dependency of modern civilization on the non-renewable energy resources such as the fossil fuels are found to have severe consequences because of the growing threat of pollution, global warming, and depleting reserves. This initiated the search for clean and renewable alternatives of the energy resources. Presently, it has become one of the most fascinating challenges for the researchers to develop various processes for energy harvesting, which can lead to a sustainable development of the society. In this direction, the advent of various renewable power resources such as solar, wind, ocean, hydropower, biomass, geothermal, and biofuels have been making significant contribution to stimulate a paradigm shift. Further, the wide use of the various types of hydrogen based fuel cells in diverse areas of technologies have shown their potential to fulfil the energy demands of the society to diminish the dependency on the fossil fuels. However, some of the major challenges associated with the development of solar cells are the improvement of the efficiency as well as miniaturization of the prototypes while for the fuel cells the major challenges lie in the production of pure hydrogen at a lower cost. The present thesis ushers a few pathways to achieve these targets.

It is now well known that two thirds of the surface of our globe is covered with sea water and splitting of the same under electric field can be one of the cleanest ways to produce hydrogen and oxygen. However, the commercial utility of this process is rather limited owing to the use of costly electrical energy apart from the economics associated with the separation of the pure hydrogen and oxygen from the oxy-hydrogen gas. However, the other naturally abundant resource in the form of solar energy is converted into electrical one with the help of solar cells, which can be employed not only for economic water splitting but also for the production of pure oxygen and hydrogen. In addition, the same electrical energy produced by the solar cells can be employed to bind the naturally abundant carbon dioxide and sea water into organic products emulating the naturally occurring photosynthesis process. Further, one of the most pertinent question in the direction of the solar cells is the effect of miniaturization in their

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efficiencies. Of late, a number of research work have shown that rather than developing top-down roll-to-roll inorganic solar cells, the bottom-up of a very large scale integration (VLSI) of an array of micro or nano solar cells can be an efficient alternative in improving the efficiency of the solar cells through process intensification.

In the past few decades, the specialities of micro or nanotechnology have also been employed in various other industrial products and processes owing to their higher efficiency as compared to their macroscopic counterparts. For example, microreactors are designed as very small volume continuous flow reactors with typical channel diameters ranging from 10 μm – 800 μm . Microfluidic reactors have now been employed in the diverse areas of technology and industries which include fine chemicals, biomedical, pharmaceuticals, electronic circuitry, sensors, and environmental remediation, among others. The microfluidic reactors are considered superior to the macroscopic analogues owing to, (a) availability of high surface to volume ratio; (b) smaller throughput leading to easier control on the operating parameters; (c) reduction in operating cost of the processes where costly chemicals are in use; (d) lower residence times; (e) easier product collection; and (f) lower energy consumption. Micro technologies are also extending their usability in the fields of fuel and energy because a VLSI of an array of efficient microreactors can lead to the process intensified advanced flow reactors having similar throughput as compared to their macroscopic counterpart at a higher efficiency.

In the present thesis, we report the development of micro and nano devices, which can be employed for the different types of clean energy harvesting. For example, (i) production of pure hydrogen and oxygen for fuel cells through microfluidic electrolyzers where the electrical energy obtained from the photovoltaic (PV) cells split water, (ii) binding of solar energy into chemical one thorough the conversion of carbon dioxide and water mixture into organic products emulating the photosynthesis process, and (iii) development of the VLSI of micro/nano solar cells to convert solar energy into the electrical one. In view of the above, the major research objectives are laid down in the following manner:

- In the beginning, we familiarise the motivation behind doing these problems in the general introduction.
- In the second chapter, we study about the microfluidic electrolyzers for production and separation of hydrogen from sea water using naturally abundant solar energy.
- In the third chapter, we develop the graphite/RGO coated flexible microscale paper-electrolysers integrated with solar cell for the membraneless production of pure hydrogen and oxygen.
- In the fourth chapter, we develop an integrated microfluidic-MEMS CO₂-sequestration device to produce essential organic products, emulating photosynthesis.
- In the fifth chapter, we develop spin-dewetted conducting polymer droplets for the process intensified VLSI of micro/nano solar energy harvesters.
- Finally, we summarize the thesis with important conclusions for the work and with the future scopes of research.

Chapter 2: Microfluidic Electrolyzers for Production and Separation of Hydrogen from Sea Water using Naturally Abundant Solar Energy

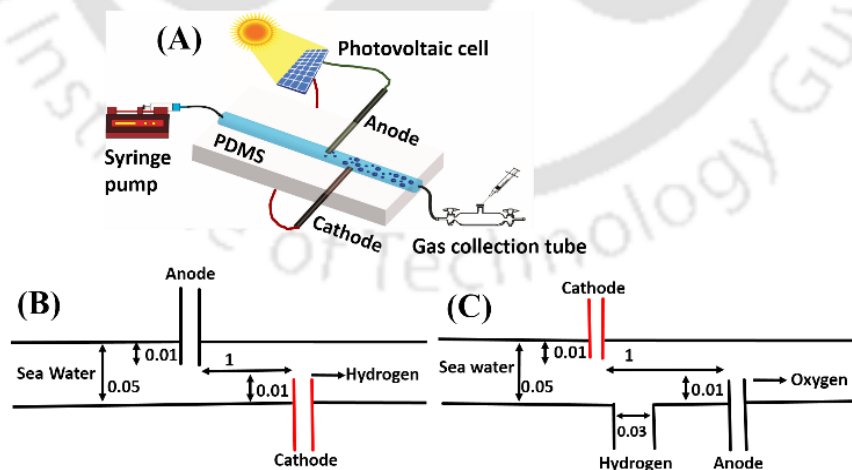


Figure 1. shows the schematic diagrams of, (A) experimental setup showing PDMS microfluidic electrolyzer (B) straight-channel microfluidic electrolyzer without separator; and (C) straight-channel microfluidic electrolyzer with separator. All dimensions shown on the image are in cm.

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In this chapter, we demonstrate a proof-of-concept polymeric microfluidic electrolyzer, (as shown in the **Figure 1**) in which hydrogen was synthesized as well as separated using the naturally abundant resources such as sea water and solar energy. In this study, initially, a microchannel was fabricated with a pair of metal electrodes inserted into it. Thereafter, the electrodes were integrated with a series of PV cells to supply high intensity direct current electric field inside the microchannel. Following this, when the sea water was flown through the channel, the electrical energy generated from the PV cells under direct solar illumination could rapidly split water into hydrogen and oxygen inside the microfluidic electrolyzer.

A simple modification in the geometry of the microchannel by fabricating an outlet at the opposite side of the cathode led to an in situ separation of hydrogen from oxygen. Further, performing the electrolysis of sea water inside a Y-shaped microfluidic electrolyzer with the electrodes integrated to the Y-arms showed an even simpler way to separate both hydrogen and oxygen in parallel to electrolysis of water. The electric field intensity developed inside the microfluidic electrolyzer also helped in developing discrete gas-liquid flow patterns with higher surface to volume ratio, which led to a larger throughput of the products. The methodology was simple to implement, capable of rapid and continuous production of hydrogen under direct solar illumination, and the rate of production could easily be tuned by controlling the flow rate of the water or applied field strength. Most importantly, the method could easily address the issues related to the cost-effectiveness of electrolyzers because the naturally abundant solar radiation illumination and sea water were employed for the electrolysis process. As compared to the similar macroscopic analogues, the proposed microfluidic electrolyzer required a much lower power for rapid electrolysis of water because the small distance between the electrodes led to; (a) a high intensity electric field and current; and (b) a lower electrical resistance between the electrodes. The micro-very-large-scale-integration (μ -VLSI) of the prototypes is expected to scale up the production matching with their macroscopic analogues. Notably, most of the commercial

electrolysis processes usually operate at elevated pressure (~6-200 bar) and/or temperature (~70-90°C), which also reduces their cost-effectiveness. In comparison, the proposed methodology was capable of producing hydrogen under ambient conditions.

Chapter 3: Graphite/RGO Coated Flexible Microscale Paper-Electrolysers Integrated with Solar Cell for the Membraneless Production of Pure Hydrogen and Oxygen

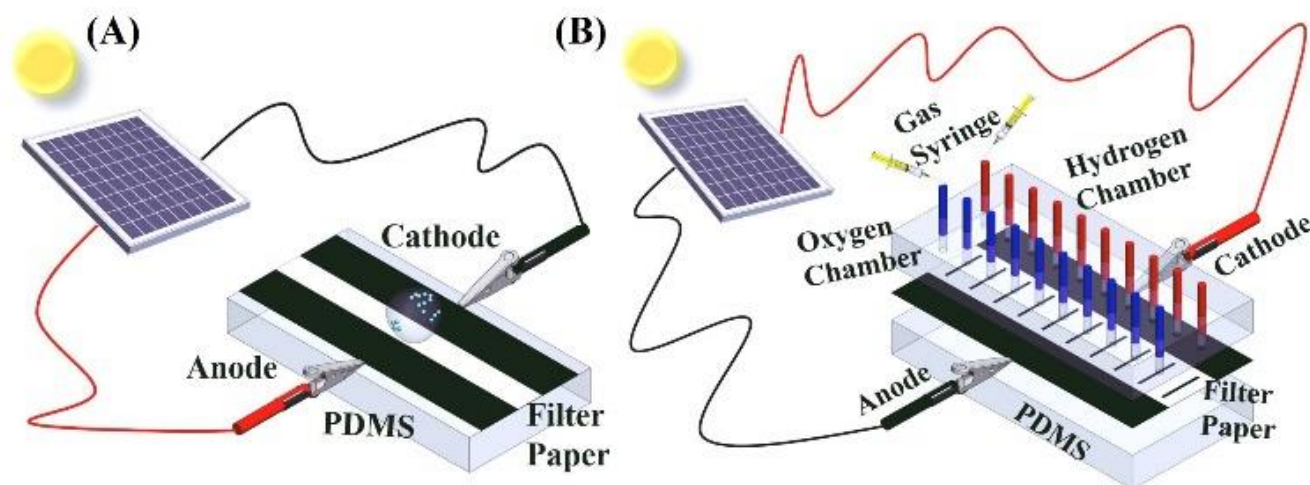
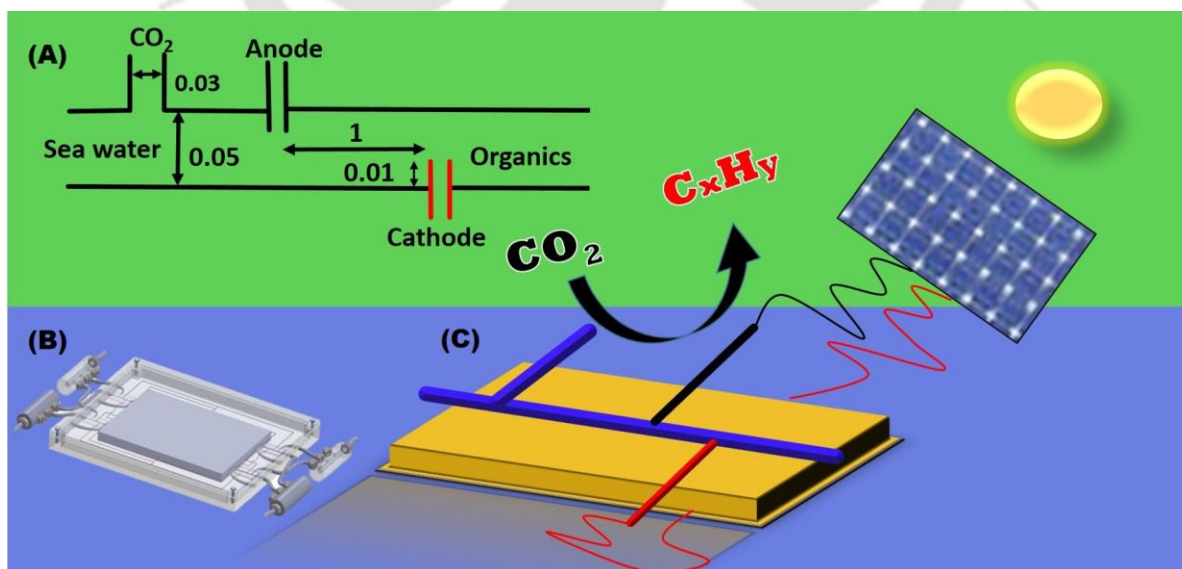


Figure 2. (A-B) show the schematic diagram of paper based ‘open’ microelectrolyzer (OME) and ‘close’ microelectrolyzer (CME) respectively for the production H_2 and O_2 .

In this chapter, we report the design and development of a pair of flexible microfluidic electrolyzers composed of graphite and reduced graphene oxide coated paper electrodes, as shown in the **Figure 2**, which could electrolyze sea water into oxygen and hydrogen when integrated with photovoltaic cell under direct solar illumination. In the ‘open’ microfluidic electrolyzer (OME) setup, initially, a microchannel was drawn on a filter paper with the help of repeated rubbing of pencil tip graphite along the sides of the open channel. Following this, a sea water droplet was dispensed on the open microchannel at the junction of the graphite electrodes before the PV cell was integrated to supply current. In such situation, the microscale width of the channel could generate a high intensity electric field even at a lower PV cell voltage, which facilitated the droplets to electrolyse into hydrogen and oxygen gases near the cathode and anode. The rate of production of these gases increased with the

increase in the field intensity. As compared to OME, in the ‘close’ microfluidic electrolyser (CME), the paper decorated with graphite electrodes was covered with a poly-dimethyl siloxane (PDMS) substrate embedded with microchannels before the electric field was applied through the PV cells. The microchannels were placed closer to the anode and cathode, which helped in the separation of hydrogen and oxygen gases after they were synthesized near the cathode and anode. The typical hallmarks of the proposed electrolyzers were, (i) use of paper and PDMS as substrates and graphite as electrode material enabled the fabrication of a flexible and metal-free microelectrolyzer; (ii) use of the microfluidic channel facilitated the water-splitting at much lower applied voltage, which recorded a typical efficiency of 1 – 2 % which was found to increase with the increase in the field intensity; (iii) use of multiple separation channels in the CME setup for production and separation of hydrogen and oxygen gases showed the potential of the proposed proof-of-concept prototype for large scale production of these gases upon μ -VLSI; (iv) the prototype could easily be integrated with other metal-free electrodes such as the reduced graphene oxide (RGO) as alternative material for graphite.

Chapter 4: Integrated Microfluidic-MEMS CO_2 -Sequestration Device to Produce Essential Organic Products, Emulating Photosynthesis



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Figure 3. (A) shows the schematic diagram of the straight-channel microfluidic electro converter. (B) shows the schematic diagram of the electro converter device. (C) shows the schematic diagram of the experimental diagram which converts carbon dioxide into organics. All dimensions shown on the image are in cm.

In this chapter, we report the development of a microfluidic reactor for continuous production of organic products from the greenhouse gas carbon dioxide and sea water employing the electrical energy produced from the solar cells, as shown in the **Figure 3**. The microreactor comprised of a polymeric substrate with a centrally embedded microchannel having a pair of inlets for carbon dioxide input and sea water input into the central microchannel and an outlet for withdrawal of the produced organic products from microchannel. An electrode assembly was embedded inside the polymeric substrate having a pair of electrodes arranged in series and integrated with the central microchannel ensuring direct contact of electrodes with the carbon dioxide gas and the sea water mixture while they were flown through the central microchannel. Integration of the solar cell with these electrodes helped in generating a high intensity electric field across the electrodes at a lower voltage to produce the organic products from the carbon dioxide and the sea water. The microfluidic reactor was capable of converting the carbon dioxide and sea water mixture into an array of essential organic products such as aldehyde, formate salts, formic acid, primary or secondary alcohols, and hydrocarbons under the influence of externally applied electric field through the solar panel, when exposed to solar irradiation. The proposed device was an environmental benign and clean energy source; as costly electrical energy was generated through solar panel which helped reducing greenhouse gas emission. A μ -VLSI of the proposed microfluidic reactors was expected to match macroscopic processes in future. Further, the use of the greenhouse gas carbon dioxide as reactant to produce commercially important organic products opened up the avenue for carbon-dioxide-sequestration, which might have far reaching consequences in mitigating global warming.

Chapter 5: Spin-dewetted Conducting Polymer Droplets for the Process Intensified VLSI of Micro/Nano Solar Energy Harvesters

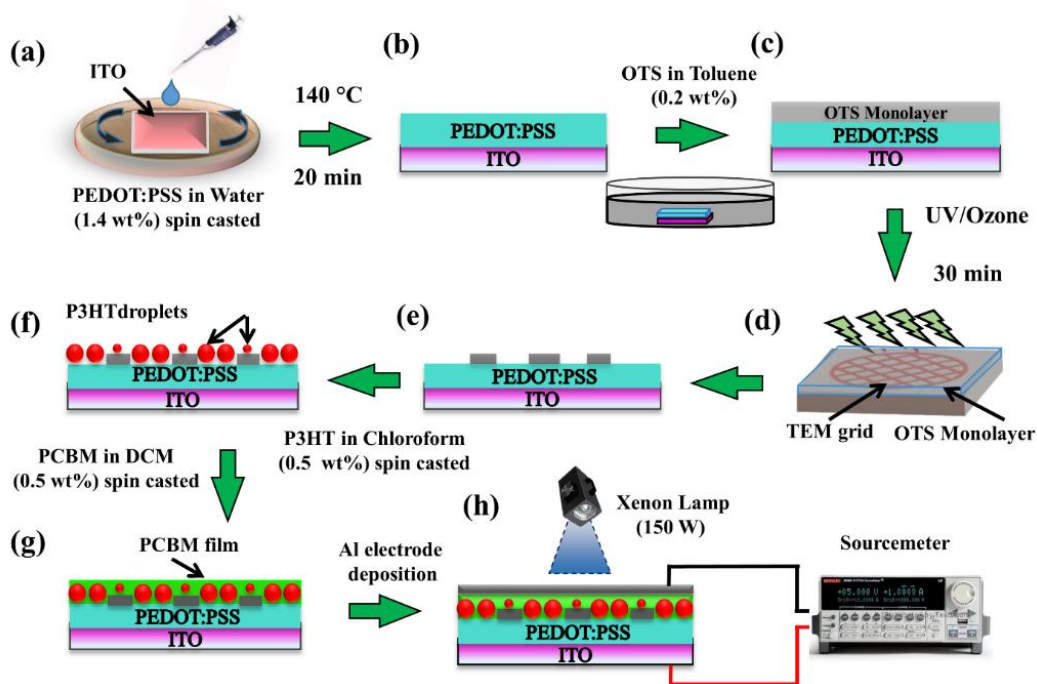


Figure 4. Shows the schematic diagram of the fabrication of spin dewetted organic solar harvesters.

In this chapter, we show the assemblage of a polymer solar cell composed of conductive polymers for improved performance. For this purpose, initially, an ITO glass was coated with a transparent thin film of the hole-collector conductive polymers, PEDOT: PSS – poly-(2,3-dihydrothieno-1,4-dioxin): poly-(styrene-sulfonate). Thereafter, a physicochemical pattern of the self-assembled monolayer (SAM) of octadecyl-trichloro-silane (OTS) was fabricated on the PEDOT: PSS film. Following this, a large collection of discrete micro or nanodroplets of the donor polymer P3HT – poly (3-hexylthiophene-2,5-diyl), were spin-dewetted on the patterned PEDOT: PSS surface before coating the acceptor PCBM – [6,6]-phenyl-C61 butyric acid methyl ester and Al electrodes on the discrete and nanoscopic P3HT droplets. **Figure 4** shows the typical steps employed to assemble numerous nano/micro heterojunctions to form an idealized bulk heterojunction (BHJ) solar energy harvester

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employing the spin-dewetted P3HT droplets. In the process, we present a detailed parametric analysis of the role of spin-speed and P3HT loading in the solvent during spin-casting on the size and the density of the P3HT droplets fabricated on the PEDOT: PSS surface. The discretization of the charge carrier donor-acceptor interface enabled the enhancement of the photoconversion efficiency via separation of photon absorption and carrier collection pathways. The study uncovers the importance of developing high-density and large-area nanopatterns in improving the performance of the solar cells. The results obtained from the VLSI of the spin-dewetted discrete solar energy harvesters were compared and contrasted with the conventional planar thin film based polymer solar cells to establish the importance of the proposed way of fabrication of the solar cells for a better performance. The results reported can be of significance in the development of the next-generation energy harvesters for binding solar energy with a higher efficiency at an optimal cost.

Chapter 6: Summary and Future scopes

In summary, the thesis deals with a number of unexplored problems associated with the clean energy harvesting employing micro and nano devices. In chapter 2, we have devised a unique method of fabrication closed microfluidic reactors using swing needles and then sea water (electrolyte) was flown through the fabricated microchannel. The electrical energy generated from the PV cells under direct solar illumination could rapidly split water into hydrogen and oxygen. A simple modification in the geometry of the microchannel by fabricating an outlet at the opposite side of the cathode led to an in situ separation of hydrogen from oxygen. Performing the electrolysis of sea water inside a Y-shaped microfluidic electrolyzer with the electrodes integrated to the Y-arms showed an even simpler way to separate both hydrogen and oxygen. In the chapter 3, we have shown the paper based flexible microfluidic electrolyzers composed of graphite and reduced graphene oxide coated paper electrodes, which could electrolyse sea water into oxygen and hydrogen when integrated with photovoltaic cell

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under direct solar illumination. We have also shown paper based ‘open’ and ‘close’ microelectrolyzers where the separation of hydrogen and oxygen can be done. In the chapter 4, we have shown a microfluidic-MEMS reactor for continuous production of organic products from the greenhouse gas carbon dioxide and sea water employing the electrical energy produced by the solar cells when integrated with photovoltaic cell under direct solar illumination. In this work, we have performed carbon dioxide sequestration with the help of the electrical energy produced from a solar cell to an array of specialty organic products. In the chapter 5, we have shown a spin-dewetted discrete solar energy harvesters which can provide better efficiencies and better performance when compared to the conventional planar thin film based polymer solar cells. This also can significant in the development of the next-generation micro batteries.

As future scopes, the hydrogen and oxygen gases produced can be employed to the fuel cells for energy production while a scale up of these processes can be attempted through μ -VLSI. Further, the hydrogen and oxygen gases produced can be directly integrated to the artificial photosynthesis process. The carbon dioxide sequestration problem can be extended to obtain product-on-demand mode in which specific organics is expected to be obtained at specific applied voltage. Again, a scale up of these processes can be attempted for through μ -VLSI. The spin dewetted solar batteries could be synthesized under controlled environment chambers such as the glove boxes or the clean rooms for their improved efficiency. Further, the concept can also be extended for other hybrid or Perovskite solar cells with improved efficiency.

Journal Publications

- (1) Investigation of Extraction of 4-Oxopentanoic Acid by N, N-Dioctyloctan-1-amine in Six Different Diluents: Equilibrium Study, Sushil Kumar, Hasan Uslu, Dipaloy Datta, **Saptak Rarotra**, and Kusuma Rajput. J. Chem. Eng. Data, 2015, 60 (5), 1447–1453. DOI: 10.1021/je501154g. (Impact factor: 1.835, ISSN-0021-9568)

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- (2) Microfluidic Electrolyzers for Production and Separation of Hydrogen from Sea Water using Naturally Abundant Solar Energy, **Saptak Rarotra**, Tapas Kumar Mandal and Dipankar Bandyopadhyay. Energy Technol., 2017, 5, (1–11). DOI: 10.1002/ente.201600512. (Impact factor: 2.557, ISSN-2194-4288).
- (3) Graphite Coated Paper Microelectrolyzers for Pure Hydrogen Production. **(manuscript under preparation)**
- (4) Integrated MEMS-Microfluidic CO₂-Sequestration Device to Produce Essential Organic Products, Emulating Photosynthesis. **(manuscript under preparation)**
- (5) Formic acid-driven ferrobots for efficient hydrogen production and energy generation **(manuscript under preparation)**
- (6) Spin-dewetted Conducting Polymer Droplets as Micro/Nano Solar Energy Harvesters. **(manuscript under preparation)**

National Patents

- (1) A Micro-Reactor and Microfluidic Electrolyzer for the Production and Separation of Hydrogen/Oxygen.
- (2) A Microfluidic- Reactor for Continuous Production of Organics from Carbon Dioxide and Sea Water.

International Patents

- (1) A Micro-Reactor and Microfluidic Electrolyzer for the Production and Separation of Hydrogen/Oxygen.

Conference Papers

- (1) Presented a paper on 'BIODIESEL' at BCET 2006, Gurdaspur.
- (2) **Saptak Rarotra**, Smita Raghuvanshi, "Laboratory Scale Development of Isothermal Bio Filter Column and Its Application for Removal of Dichloromethane". International Conference CHEMCON 2011, Bangalore.
- (3) **Saptak Rarotra**, and Kusuma Rajput and Sushil Kumar," Application of Ionic Liquids in the Extraction of Organic Acids: A Brief Review. TACEE 2012, BITS Pilani, Pilani.
- (4) **Saptak Rarotra**, Tapas Kumar Mandal, Dipankar Bandyopadhyay, "Electrolytic Production of Hydrogen Energy by Water-Splitting in Polymer based Micro reactors". Flow Chemistry India, SELECT BIOSCIENCES, CSIR-IICT, Hyderabad, India 2014 (Best Poster Awarded).

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- (5) **Saptak Rarotra**, Tapas Kumar Mandal, Dipankar Bandyopadhyay, "Field induced Conversion of CO₂ and Sea Water into Organic Products inside a Microfluidic Reactor. International Conference on MEMS and Sensors (ICMEMSS), Indian Institute of Technology Madras, Chennai, INDIA 2014.
- (6) Amit Kumar Singh, Seim Timung, Divesh Ranjan, **Saptak Rarotra**, Tapas Kumar Mandal and Dipankar Bandyopadhyay, "Vinegar driven micro motors for nanoparticle synthesis". Emerging Materials: Characterization & Application, CSIR-CGCRI, and Kolkata, India 2014.
- (7) Mitradip Bhattacharjee, Nilanjan Mandal, Satarupa Dutta, **Saptak Rarotra**, Harshal B. Nemade, Tapas Kumar Mandal and Dipankar Bandyopadhyay, "Controlled Drug Release: Attachment of Drugs on Magnetic Nanoparticles". International Conference on Translational Nano medicine T-NANO, Ahmedabad, India 2014.
- (8) Mitradip Bhattacharjee, **Saptak Rarotra**, Dipankar Bandyopadhyay," Change in optical absorption of CdS nanoparticles due to microwave assisted annealing". Proceedings of the India International Science Festival- Young Scientists' Meet. Department of Science and Technology, Government of India – Dec 4-8, 2015 held at Indian Institute of Technology Delhi.
- (9) **Saptak Rarotra**, Tapas Kumar Mandal, Dipankar Bandyopadhyay," Vindicated use of Microfluidic technology in Energy harvesting." CHEMCON 2016, Indian Institute of Technology, Guwahati India 2016.
- (10) Surjendu Maity, **Saptak Rarotra** and Dipankar Bandyopadhyay, "Field Induced Enhanced Productivity of Multiphase Microfluidic-Reactor". 3rd Indo German workshop, Indian Institute of Technology, Guwahati India 2016.
- (11) **Saptak Rarotra**, Mitradip Bhattacharjee, Dipankar Bandyopadhyay," Change in optical absorption of CdS nanoparticles due to microwave assisted annealing". International conference on functional materials (ICFM 2016) Dec 12-14, 2016 held at Indian Institute of Technology Kharagpur, India.
- (12) **Saptak Rarotra**, Tapas Kumar Mandal, Dipankar Bandyopadhyay, "Electrolytic Production of Hydrogen Energy by Water-Splitting in Polymer based Micro reactors". 5 th Symposium on Advanced Biological Inorganic Chemistry (SABIC2017) January 07-12, 2017 organized by TIFR and IACS in Kolkata, India.
- (13) **Saptak Rarotra**, Shahid Sheikh, Tapas Kumar Mandal, Dipankar Bandyopadhyay, "Carbon based photo catalysts for water splitting inside microreactors"3rd Reflux, Indian Institute of Technology, Guwahati India 2017.