Development of Model Synthetic Leaf to Harvest Light

Funding Agency	DST-SERB
Sanctioned Amount	Rs. 40.20 Lakhs
Project Duration	3 Years
Project Status	Completed

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Brief Description of the Project

1. Development of synthetic systems harvesting sunlight
2. Fixation of carbon dioxide
3. Hydrogenase mimics
4. Charge storage device
5. Reactive oxygen species (ROS)

Methodologies/Approaches Adopted

Nature performs an astonishing range of selective syntheses and transformations of both organic and inorganic systems and, what is more, it achieves this under ambient conditions. It is not surprising, therefore, that our research group strives to understand and emulate natural chemical processes through "bioinspired" and "biomimetic" chemistry. Plants store hydrogen by reaction with carbon dioxide to form carbohydrates.

Based on our experience with natural chlorophylland with synthetic porphyrins necessary metallation were made.Derivatized zinc and magnesium A_3B porphyrins function like chlorophylls or bacteriochlorophylls (present is light harvesting scaffolds).

Fixing of carbon dioxide to get the thermodynamically difficult step to reduce it to formate hass been made but the systems requires modification to enhance rate.

Some models of hydrogenase based on our report (highlightedas better than nature, using asymmetric dithiolene complexes and clusters of transitions metal ions (M=Ni, Fe, Cu) which can function like plastocyanin $(Cu(N\text{-}His)_2(S\text{-}Meth)(S\text{-}Cys)$, hydrogenases(Ni/Fe or Fe/Fe) or iron-sulfur$[Fe_xS_y]^{n-}$ proteins. We have envisaged a process to develop acetylene derivatised A_3B Zn/Mg porphyrin wherein the acetylene moiety can be cycloadded to S_4 of $[M(S_4)_2]^{n-}$; $[M(S_4)(bpy)]$ to form dyads. Such dyad is used to study photoinduced electron transfer reaction and their ability to produce hydrogen under visible light. At an initial phase the ability of metal dithiolene complexes to function as electro catalyst for HER (hydrogen evolution reaction) is being explored.

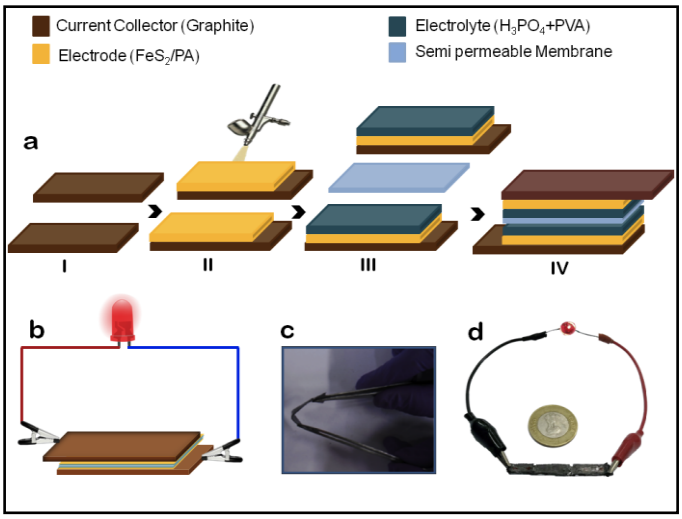
The ability of carboxy-derivatised porphyrin to bind semiconducting metal oxides inspired us to tether amino-porphyrin with carboxylated water soluble carbon nano-onions (wsCNO's) interestingly our hybrid is water insoluble. In addition, for heterogeneous HER reduced graphene oxides are being doped with molybdenum disulfide;

Development of rGO coated microscopic slides having low resistance.

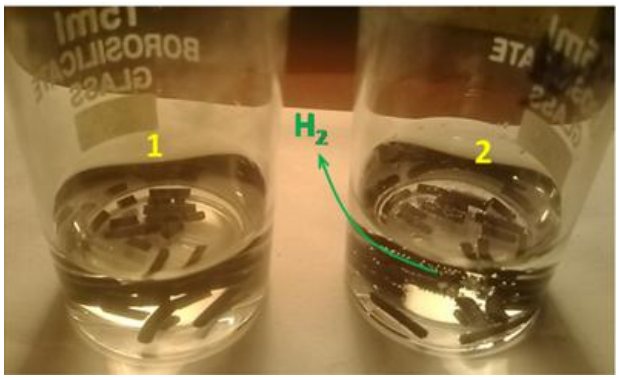
Sustainable charge storage devices that are environmentally benign, readily moldable, easily synthesizable, and profitable for applications in electronics industry are tried.

Project Highlights

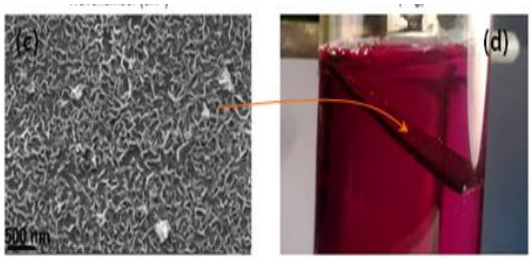
Iron pyrite (FeS_2) ,which is one of the primitive chemicals responsible for the evolution of life, is used in photo-voltaic devices and also in seed dressing in agriculture. An innovative application of nano FeS_2 as a symmetric charge storage device that is flexible, portable, light weight; along with its fabrication has been made . In its present laboratory prototype form; it powers solid-state electronic devices and electric motors. Further refinements of this device will open new avenues in the field of sustainable charge storage devices and low power electronics.



Porphyrin as composite materials with graphene and or MoS_2 may be rightly used to trap sunlight and produce hydrogen. We processed graphene, nano-MoS_2 using cheap synthetic route and preliminary observations are encouraging.



1. Molecular Sieves coated with rGO; MoS_{2+x}; in deionised water containing triethanolamine. 2) Molecular Sieves coated with rGO; MoS_{2+x}; Mg-Pthalocyanine in deionised water containing triethanolamine pH=10. Both the tubes are under light exposure where only **2** shows clear evolution of hydrogen.

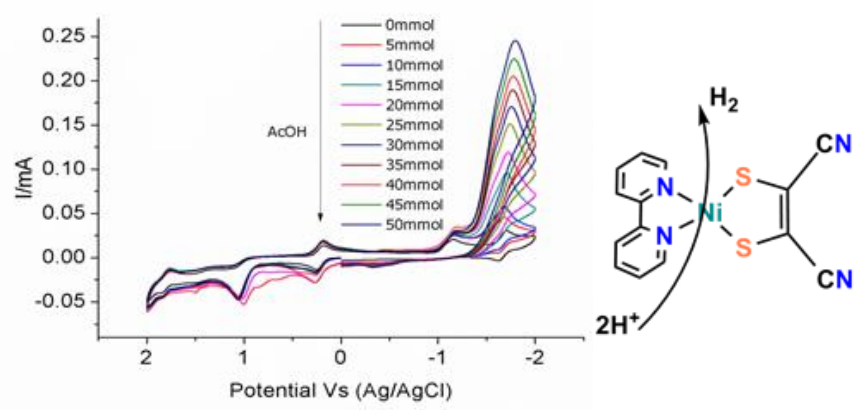


(c) SEM image of synthesized two dimensional sheet of MoS_2 d) Shows bubbles of H_2.

Oxygen and Reactive Oxygen species

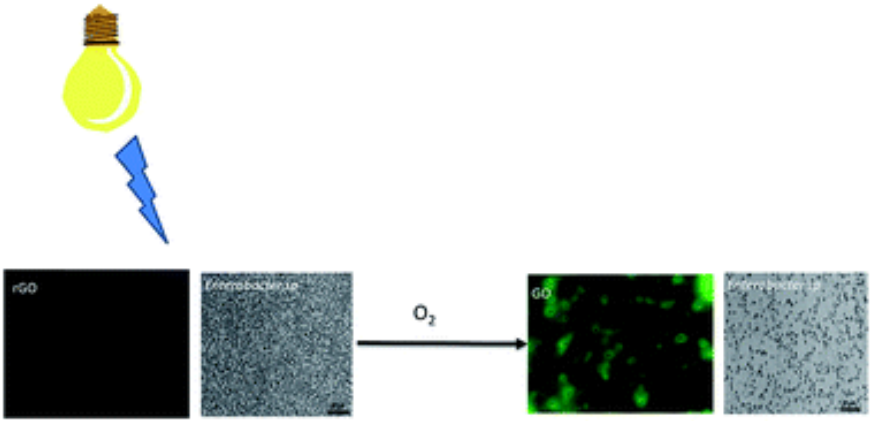
MgTPP is susceptable to oxidative degradation in the presence of light but photophysical studies λ> 400nm show that the photodegradation of MgTPP in the presence of azide is restricted under oxygen and visible light. Interestingly the analogous psuedohalide thiocyanate is unable to inhibit the degradation under similar conditions. Azide ions or histamine mimic the coordination of histidine to chlorophylls and also its role as a singlet oxygen quencher.

Hydrogenase

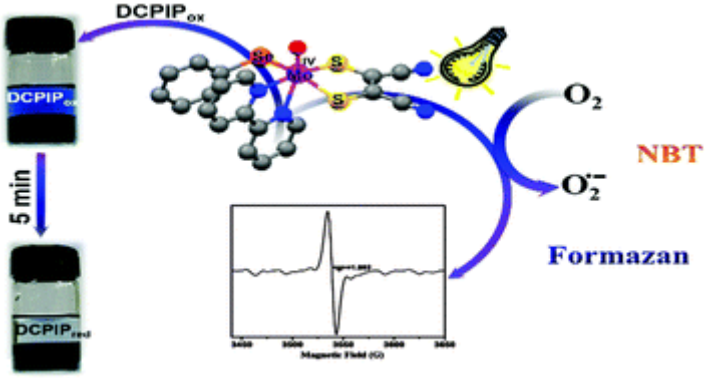


Cyclic voltammograms of **[Ni(bpy)(mnt)]** (0.5 mM) in CH_3CN/H_2O without the presence of acid (black) and in the presence of acetic acid with increasing concentration (other colors). Conditions: 0.1 M $NaNO_3$, glassy carbon as working electrode, scan rate 50 mV/s.

Reduced graphene oxide (rGO) generates reactive oxygen species (ROS) under visible light in air *via* a singlet oxygen–superoxide anion radical pathway which readily kills *Enterobacter* sp. GO is not toxic but on ageing it gets a surface coating of rGO and shows toxicity. This can be used to combat hospital pathogens

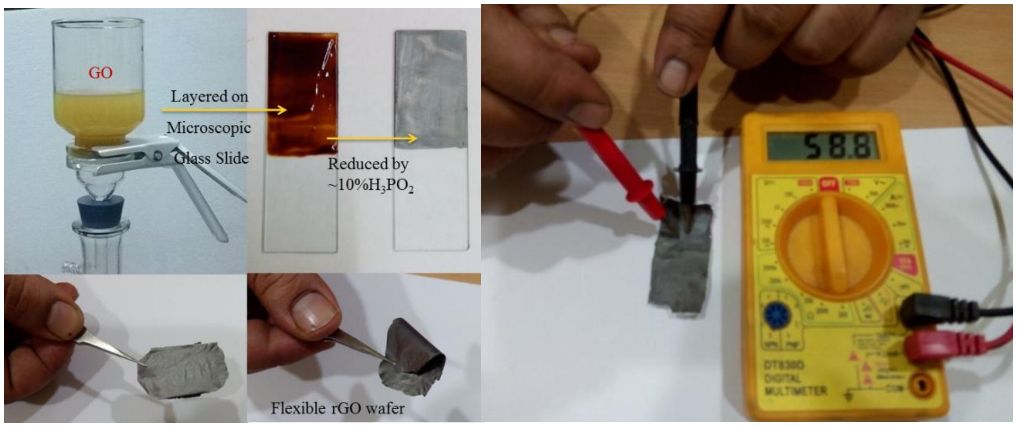


$[NBu_4][MoO(bpy)(mnt)(SePh)]CH_2Cl_2$(1)and $[NBu_4][MoO(phen)(mnt)(SePh)]CH_2Cl_2$ (2) complexes; (bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, mnt = maleonitriledithiolate ion) stabilized by aromatic diimine have been synthesized and characterized. These complexes under aerobic conditions on irradiation with sunlight (or with light from a tungsten lamp) in solution generate superoxide radicals concomitant to the formation of paramagnetic Mo(V) species due to a single electron transfer from the Mo(IV) complex to oxygen. The Mo(V) produced under photo-irradiation was characterized by EPR spectroscopy and the generated superoxide radical has been shown to transform nitrobluetetrazoleum (NBT) chloride to blue diformazan. Both 1 (and 2) are phosphorescent having an emission lifetime of 6–8 μs. Ground state and time dependent density functional theoretical calculations confirm that the electronic transitions from predominantly metal based molecular orbitals are responsible for the low-lying charge transfer excited states and also for the observed interaction with oxygen.



Project Achievements

Innovations: Replacing ITO with rGO coated on membrane a reality



Application Potential:

Long Term

Patentable composite materials using porphyrin and graphene can be made under the present project to trap solar energy.

The MoS_2 can be deposited on rGO (reduced graphene oxide) to make photocathodes that can be shorted with OEC (oxygen evolving complex) to achieve photoinduced splitting of water.

The coordination of histidine in chlorophyll *a* has a specific which probably is to quench singlet oxygen produced by the triplet state Chl*a*. Under condition of extreme sunlight when carotenes get exhausted by singlet oxygen plant use these histidine to counter it. This quenching effect has been modelled using histamine and azide. In addition systems that are being used for photoinduced reduction of water needs to be guarded against the singlet oxygen to hinder photo-bleaching.

The acetylene derivatised porphyrin offer a new synthetic strategy to prepare porphyrin that can be connected with new dithiolene complexes.

Immediate

Some of the products are ready for implementation. rGO graphene oxides have been layered on microscopic glass slides which have shown very low resistance of 14-20ohms(not shown). This is very close to the commercially available ITO which has resistance of 15-30ohms. The rGO are doped with various p-type oxides such as Cu_2O etc. to make photoanodes.

Publications

1. Nano iron pyrite (FeS2) exhibits bi-functional electrode character, Amarish Dubey, Sushil Kumar Singh, Brindan Tulachan, Manas Roy, Gaurav Srivastava, Deepu Philip, Sabyasachi Sarkar and Mainak Das, RSC Adv., (2016), 06, 16859-16867.
2. Photoinduced Electron Transfer from Oxo-Mo IV Selenolato Complex to Oxygen, Joyee Mitra and Sabyasachi Sarkar, New. J. Chem. ,(2015), 40, 626-633.
3. ROS generation by reduced graphene oxide (rGO) induced by visible light showing antibacterial activity: comparison with graphene oxide (GO), Taposhree Dutta, Rudra Sarkar, Bholanath Pakhira, Subrata Ghosh, Ripon Sarkar, Ananya Barui and Sabyasachi Sarkar, RSC. Adv.(2015), 05, 80192-80195.
4. Involuntary graphene intake with food and medicine, Manav Saxena and Sabyasachi Sarkar, RSC Adv., (2014), 4, 30162-30167.
5. Iron pyrite, a potential photovoltaic material, increases plant biomass upon seed pre-treatment, Gaurav Srivastava, Anubhav Das, Tejas Sanjeev Kusurkar, Manas Roy, Saket Airan, Raj Kishore Sharma, Sushil Kumar Singh, Sabyasachi Sarkar, Mainak Das, Mater. Express,(2014), 4, 23-31.
6. Solid Phase Synthesis and Structural Characterization of an Oxo-molybdenum (V) Porphyrin: Triplet State ESR Spectrum of μ-oxo Bridged Molybdenum (V) Dimer, Goutam Nandi and Sabyasachi Sarkar, J. Porphyrins Phthalocyanines, (2014), 18, 282-289.
7. High Yield Synthesis of Oxo-Tungsten(V) Porphyrin: Structural Characterization of the Hydrolyzed Products, Goutam Nandi and Sabyasachi Sarkar, Inorg. Chim. Acta. , (2013), 410, 106-110.
8. NO2-induced synthesis of nitrato-iron(III) porphyrin with diverse coordination mode and the formation of isoporphyrin, Jagannath Bhuyan and Sabyasachi Sarkar, J. Chem. Sci. , (2013), 125, 1-8.

9. Magnetic and electrocatalytic properties of nano-Pd and Pt-carbon nano-onion composite, El Said A. Nouh, Manas Roy, Goutam Nandi and Sabyasachi Sarkar, Adv. Sci. Eng. Med. ,(2013), 5, 1181-1186.
10. Synthesis, Spectral and Electrochemical Studies of a Series of Oxo-Tungsten (V) Porphyrins, Goutam Nandi, Sabyasachi Sarkar, Euro. J. Inorg. Chem.,(2013), 20, 3518-3525.
11. Nitrous acid Mediated Synthesis of Iron Nitrosyl Porphyrin: pH Dependent Nitric Oxide Release, Jagannath Bhuyan and Sabyasachi Sarkar, Chem. Asian J.,(2012), 7, 2690-2695.

Press –Media appreciation

1. Easy way to fight hospital pathogens Published in **Nature, India** , **26th October, 2015**
2. Debunking the graphene myth, published in **The Telegraph,India, 14th July, 2014.**
3. Graphene oxide stands the test of time published in **Chemistry World (Royal Society of Chemistry, UK), 1st July, 2014.**
4. Barbecued gives clean chit to nano carbon published in **Nature India, 23rd June, 2014.**

Facilities Developed

New lab has been developed named "Nano Science and Synthetic Leaf Lab" at Downing Hall with UV-VIS spectro-photometer (JASCO-V630) facility.

Plan of Future Project Proposal based on the Current Project

Zinc Protoporphyrin IX a carrier of trimethylamine N-oxide that promotes Artheroschelrosis

(New project has been sanctioned by DST-SERB: EMR/2015/001328)