Graphene and its composite as solar sponge for water- splitting

Funding Agency	DST-SERB
Sanctioned Amount	Rs 24.8 Lakhs
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Project Status	Continuing since 22/10/2014

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Brief Description of the Project

It is the billion year challenge of some early living microbes in fixing carbon dioxide to create food under geothermal and finally with solar radiation since the earth has been created. These chemo auto-trophs slowly evolved as photo –autotroph like purple bacteria and cyanobacteria to trap solar energy to fix carbon dioxide using hydrogen sulfide and finally stabilized by using water. The production of reducing equivalent or hydrogen from light-driven water splitting is the product of an environmentally clean efficient natural work machine which is one of the most enthralling aspects of the current research to mimic. To develop "artificial leaf" for water- splitting various approaches are currently being made including molecular design of ligands, semiconducting inorganic nano materials with surface modification, but there are limitations in terms of cost hurdle, sustainability and catalytic efficiency and reusability.

This project aimed to catalytically produce hydrogen using visible light. Our current research led to the production of reduced graphene oxide (rGO) using ingenious inexpensive method with conductance limit similar to indium coated tin oxide glass (ITO). In addition, this rGO is stable in highly alkaline and acidic solution unlike ITO which is etched in acidic medium. This has inspired us to look at cheaper sources for isolation of graphene oxide. The composite layer of graphene and /or with varied metallo porphyrins absorbs the entire visible solar radiation. This layer may be short circuited with the ITO layered with inorganic metal oxo clusters on the opposite side. Water, as loosely attached to the metal center creating acidic proton may release electron generated by graphene/porphyrin will produce hydrogen and the oxide (hydroxide) ion from water would reach the graphene and or cationic radical of porphyrin to de-load its electron regenerating the initial state of the graphene- porphyrin composite with the evolution of oxygen and thus this will create an effective catalytic cycle.

Keywords: graphene, metallo porphyrin, metal oxo cluster, water splitting

Highlight

Heavily nitrogen doped graphene oxide (NDG) containing 15% nitrogen was obtained from non-mulberry silk cocoon membrane (Tassar, Antheraea mylitta) by pyrolyzing the cocoon at 400^0C in argon atmosphere. High resolution TEM study of NDG shows the presence of single and stacked graphene sheets with embedded amorphous mass. Cyclic Voltammetry experiment performed in 1 M H_2SO_4 showed high specific capacitance around 348 F g^{-1} at 5 mV s^{-1}.

Sustainable charge storage devices require materials that are environmentally benign, readily moldable, easily synthesizable, and profitable for applications in electronics industry. Nano iron pyrite (FeS_2) is one such material, which is applicable in diverse areas like photo-voltaic devices to seed dressing in agriculture. In this work, we propose an innovative application of nano FeS_2 viz., as a symmetric charge storage device that is flexible, portable, light weight; along with its fabrication details. The device consists of (H_3PO_4)/polyvinyl alcohol (PVA) electrolyte gel sandwiched between

two similar electrodes made up of FeS_2/poly-aniline (PA), upon which graphite sheets being used as current collectors. Electrodes were characterized by XRD, FTIR and SEM. Device was calibrated by cyclic-voltammetry and charge-discharge cycle. 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.

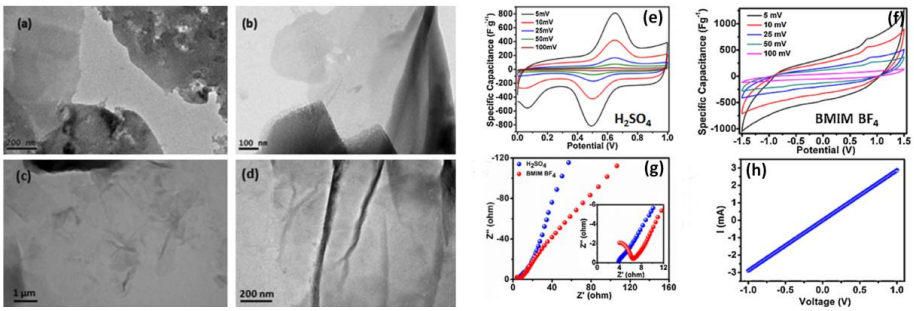

Figure 1(a) HRTEM analysis of NDG (a) crumbled and stacked NDG, (b) HRTEM images of NDG with very low stacking, (c,d) large area distribution of NDG with corrugation endorsing single layer. (a) CV of NDG in 1 M H_2SO_4 and (b) 1 M BMIM BF_4, (c). Nyquist plot of NDG in 1 M H_2SO_4 and 1 M BMIM BF_4, (d) representative I-V graph of NDG.

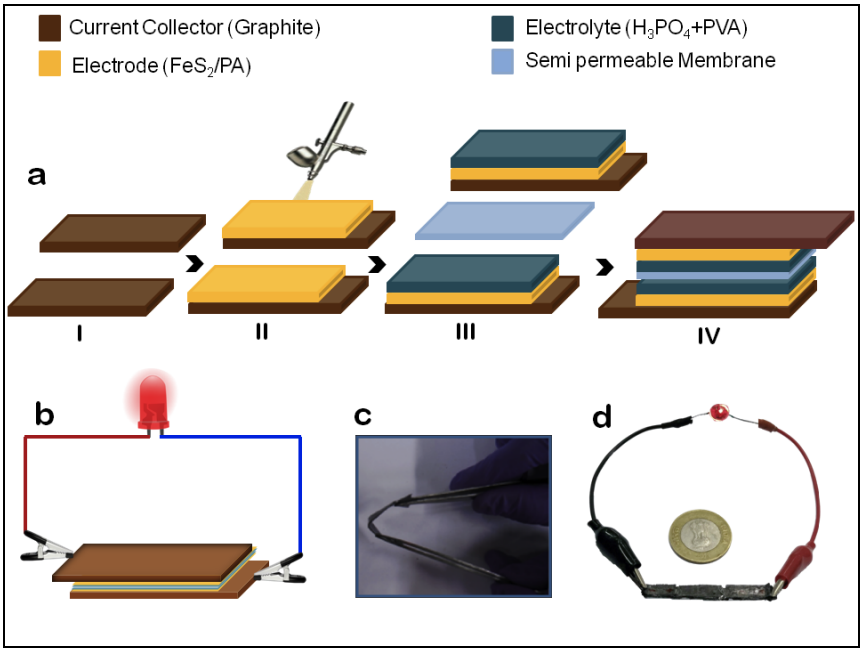

Figure 2. Architecture and assembly of the prototyped charge storage device. a. Preparation flow of charge storage device. (i). Two graphite sheets as current collectors. (ii). FeS_2/ Poly-aniline composite spray painted using an air brush onto the graphite sheets for making the electrodes. (iii). The electrolyte gel (phosphoric acid + polyvinyl alcohol) is placed on top of the electrodes. (iv). Charge storage device assembly having a semi-permeable membrane between the gel faces. b. A schematic representation of a functional charge storage device with symmetric nano FeS_2/PA electrodes connected to an LED. c. Demonstrating flexibility property of the

Publications:

1. Heavily nitrogen doped, graphene super capacitor from silk cocoon, Vikrant Sahu,Sonia Grover, Brindan Tulachan, Meenakshi Sharma, Gaurav Srivastava, Manas Roy, Manav Saxena, Niroj Sethy, Kalpana Bhargava, Deepu Philip, Hansung Kim, Gurmeet Singh, Sushil Kumar Singh, Mainak Das and Raj Kishore Sharma, Electrochim. Acta. (2015), 160, 244-253.
2. Reusable palladium nanoparticles in one-pot domino Sonogashira-cyclization: Regio- and stereo- selective syntheses of (Z)-3-methyleneisoindoline-1-ones and furo[3,2 h]quinolines in water, Rammyani Pal, Nivedita Chatterjee, Manas Roy, El Said A. Nouh, Sabyasachi Sarkar,Parasuraman Jaisankar, Swarbhanu Sarkar and Asish Kumar Sen, Tetrahedron Lett. (2016), 57, 43-47.
3. 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. Advances.(2016), 06, 16859-16867.

Facilities Developed (Equipment procured)

One Micro pO_2 measurement with data logging systems and accessories recognition