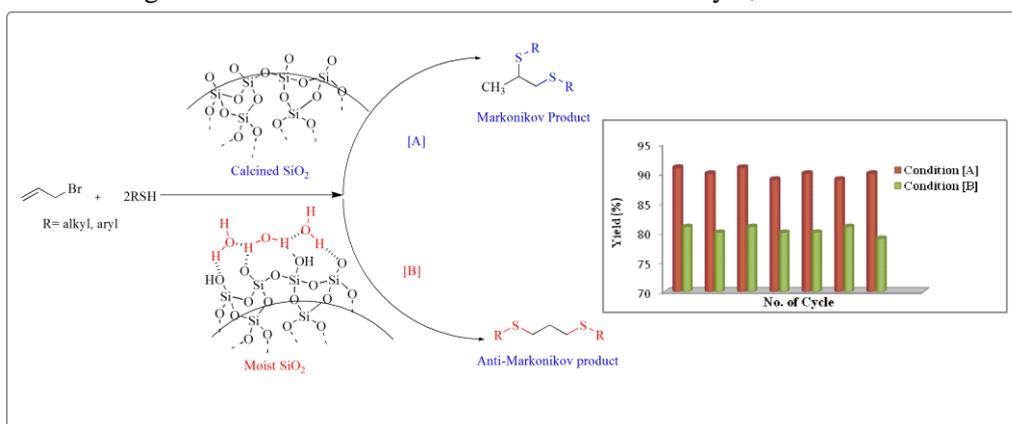


## ABSTRACT

The research work embodied in this thesis entitled “**Studies on Solid-Phase Organic Reactions & Catalysis: Greener Approaches**” was initiated in February 2009 as a CSIR–NET–JRF and became successful with the kind support of UGC for Teacher Fellowship under the scheme of ‘Faculty Development Program’. The research work is primarily motivated to develop new approaches for conducting organic reactions under greener conditions by following solid-phase techniques as well as catalysis. The entire work was emphasized on different types of solid supports mainly silica, graphene-based carbon materials and poly-ionic resins to promote various organic reactions. The thesis has been divided into five chapters.

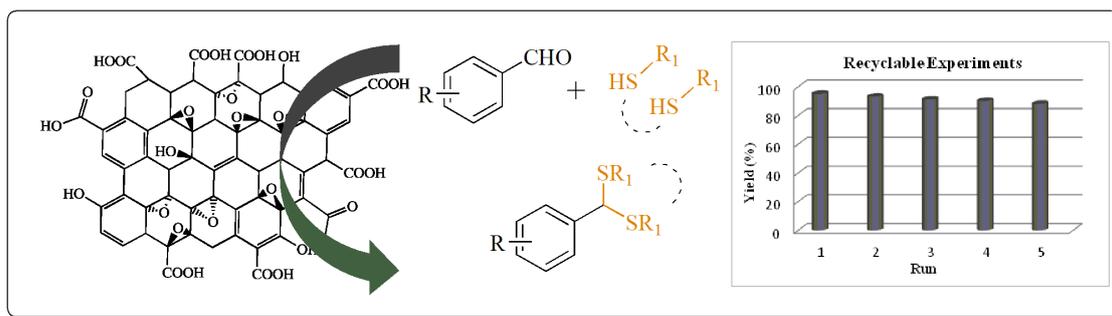
At the beginning, the **CHAPTER I** is started with a brief review mainly focusing on solid-phase organic reactions and catalysis promoted by different types of inorganic and organic solid-supports. ‘Silica gel’ which is generally used as an adsorbent in chromatography is also known as an efficient inorganic solid support to promote diverse organic reactions. Recently, graphene and graphene-based materials have attracted synthetic organic chemists due to their unusual behavior towards sustainable organic synthesis. Among various organic polymer supports, poly-ionic resins have a major role for developing diverse polymer-supported reagents and catalysts as well as metal nanoparticles which are efficient to promote solid-phase organic reactions.

**CHAPTER II** demonstrates the tuning surface behavior of silica gel under pre-calcined and moistened states to promote regioselective addition of excess thiol with allyl bromide to produce 1,2- or 1,3-dithioethers respectively. The presence of physically adsorbed water on the silica surface influenced for the anti-Markonikov addition of thiols to inactivated allylic double bond to produce 1,3-dithioether. On the hand, HBr which is produced in the first step of the reaction activate the allylic double bond and assist the sulfur atom of excess thiol to couple with the more stable secondary carbocation resulting in the Markonikov addition to form exclusively 1,2-dithioether.



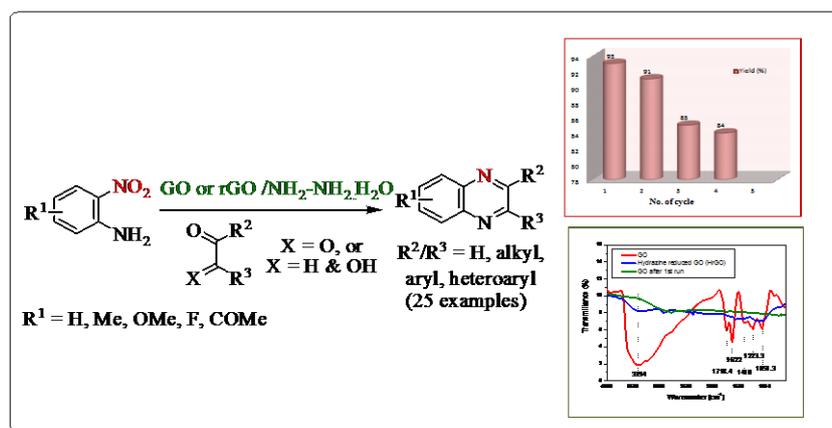
[This work entitled “Silica: An efficient catalyst for one-pot regioselective synthesis of dithioethers” has been published on *Beilstein J. Org. Chem.*, 2014, 10, 26-33]

**CHAPTER III** is divided into two sections: **Section A & Section B**. **Section A** represents an efficient and greener method for the synthesis of open chain, cyclic and unsymmetrical dithioacetals from aryl/hetero-aryl/aliphatic aldehydes catalyzed by graphene oxide (GO). The reaction conditions are mild, solvent-free and aerobic. Notable features of this methodology are operational simplicity, nil or negligible formation of disulfide, chemoselectivity, recyclability and environmental compatibility.



[The work entitled “Graphene Oxide (GO)–catalyzed chemoselective thioacetalization of aldehydes under solvent-free conditions” has been published on *Tetrahedron Lett.*, 2014, 55, 6596–6600]

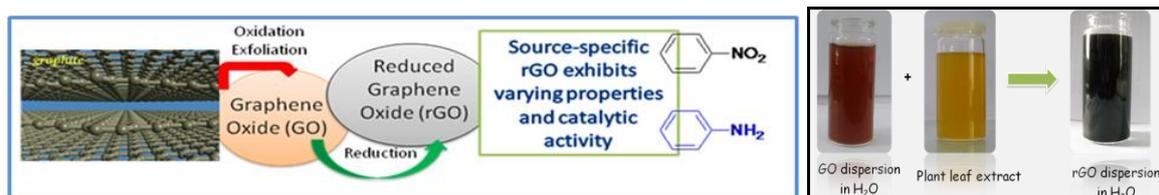
**Section B** demonstrates a straightforward and green synthesis of bio-active scaffold quinoxalines directly from 2-nitronilines *via* one-pot reduction-condensation reactions using hydrazine hydrate as the reductant and GO/rGO as the catalysts under complete metal free conditions. The catalyst has been recovered, characterized and recycled for four consecutive runs.



[This work entitled “Graphene oxide (GO) or reduced graphene oxide (rGO): efficient catalysts for one-pot metal-free synthesis of quinoxalines from 2-nitroaniline” has been published on *Tetrahedron Lett.*, 2015, 56, 6762–6767]

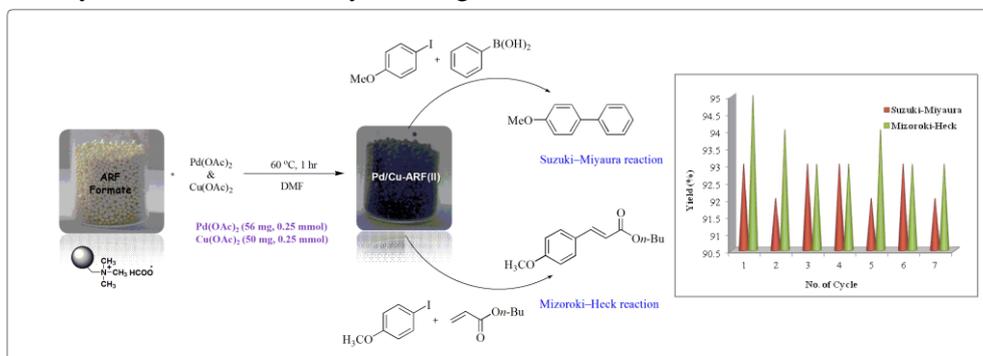
**CHAPTER IV** portrays about the comparative evaluation of diverse properties of chemically and biologically reduced graphene oxides (rGOs). Reduced graphene oxides (rGOs) can be prepared from graphene oxide (GO) by several methods and reducing sources including some phyto- and fungi-extracts. However, rGOs obtained by different methods might exhibit different properties depending on the extent of residual oxygen-containing functional groups, though textural aspects of rGOs seem to be rather similar. The present study has been aimed at making a comparative evaluation of various properties of reduced graphene oxides (rGOs), prepared by using chemical and biological reducing sources, and to establish specific reducing agent, in particular from greener sources, which might be more effective in exhibiting catalytic activity. Four different plants extracts viz. *Adathoda Vasika* (Malabar nut), *Azadirachta Indica* (Neem), *Camellia Sinensis* (Tea), *Moringa Oleifera* (Drumstick), and a fungi *Volvereilla Volvacea* (Mushroom), all are edible to human beings, and one chemical reductant (hydrazine hydrate) were used to obtain rGOs from GO. Each rGO was characterized by UV-Vis, FT-IR, Raman spectroscopic techniques, and surface morphological aspects were obtained by powder XRD, Scanning and Transmission electron microscopic images. The acidic nature (pH) of rGOs in aqueous suspension was measured with a pH meter and their

cation–exchange capacity was calculated by potentiometric titration in the presence of an electrolyte. Further, the catalytic activity of rGOs was measured in a model reduction of nitrobenzene to aniline at room temperature and monitoring the progress by UV–Vis spectroscopy. While textural aspects of various rGOs are fairly similar, various physicochemical properties like pH, cation–exchange ability etc. are found to be different for rGOs obtained by using different reductants. Moreover, there is significant variation observed in their catalytic activity in the reduction of nitrobenzene. By comparison, it was found that rGOs obtained by using plant leaf extract of *Adathoda Vasika*, (brGO–AV) and *Volvereilla Volvacea*, (brGO–VV) exhibit significantly better catalytic efficiency than others.



[This work titled “Reduced Graphene Oxides (rGOs): Source–dependent Properties and Catalytic Activity” has been communicated.]

**CHAPTER V** depicts about the catalytic applications of poly-ionic resins embedded with Pd/Cu bimetallic NPs in two most important C–C bond forming reactions, Suzuki–Miyaura and Mizoroki–Heck coupling reactions. A comparative study between monometallic Pd–ARF and bimetallic Pd/Cu–ARF towards Suzuki and Heck coupling reactions demonstrates the more catalytic efficiency of bimetallic NPs compared to monometallic Pd NPs as catalysts. The Pd/Cu–ARF bimetallic NPs have been found to be recyclable for seven consecutive runs without loss of any catalytic activity as well as without any leaching of metals.



[This work titled “Bimetallic Pd/Cu NPs embedded on macroporous ion–exchange resins: Application to Suzuki–Miyaura and Mizoroki–Heck reactions” manuscript under preparation]