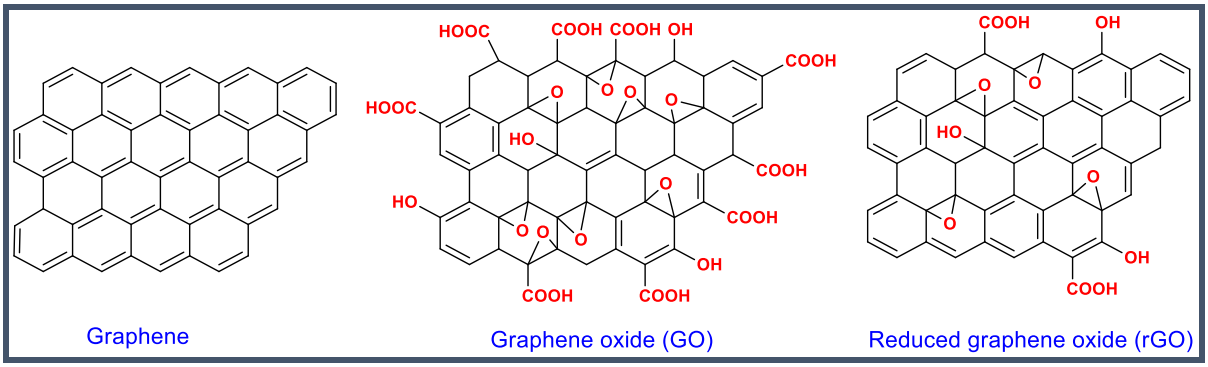
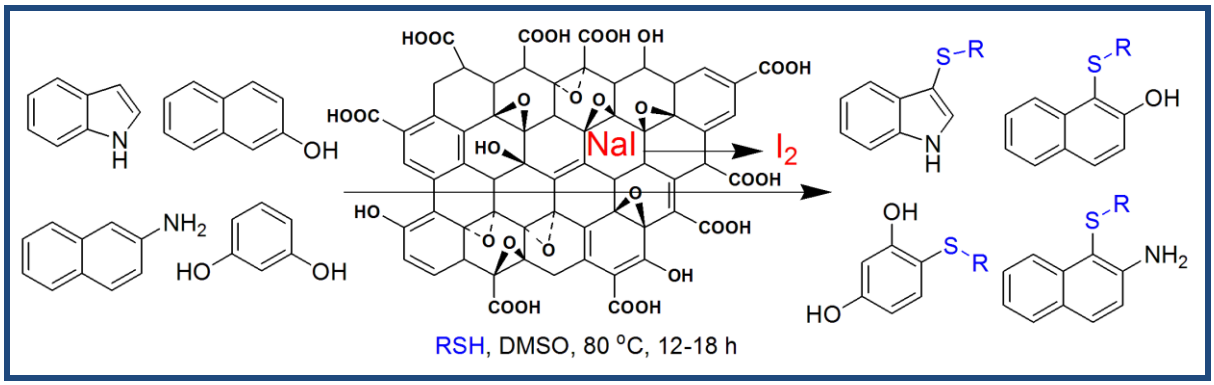
ABSTRACT

The present thesis entitled "**CARBONACEOUS NANOMATERIALS AND COMPOSITES: GREEN TECHNIQUES FOR ORGANIC SYNTHESIS**" mainly focuses on the design and catalytic applications of graphene-based nanomaterials in organic synthesis. The development of graphene-based materials like graphene oxide (GO), reduced graphene oxide (rGO), CNTs, etc., has been an emerging area of research. Graphene and functionalized graphenes possesses unique structural properties which led to their wide application in frontier areas of chemistry and material science. In this thesis I have focused on the preparation and catalytic applications of functionalized graphenes and metal supported graphene-based nanocomposites. The thesis is divided into two chapters and those chapters are further subdivided into different sections as outlined below.

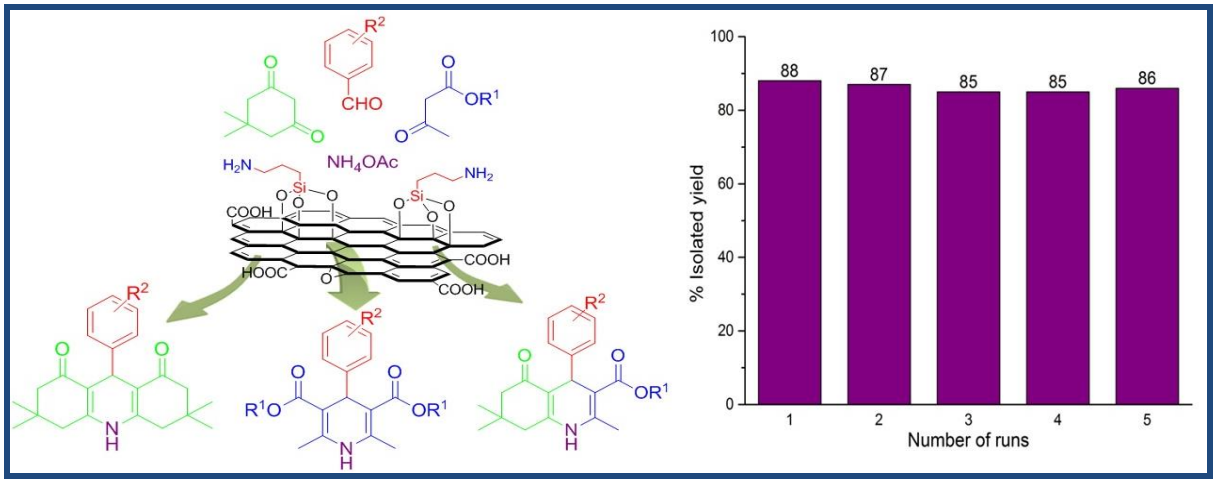
Chapter I has been divided into four parts. **Section A** presents a brief review on carbonaceous nanomaterials. The origin and advancement in the field of carbonaceous nanomaterials like graphene, fullerenes, CNTs, etc., have been highlighted. The two main routes for the functionalization of graphene have been briefly discussed. Different approaches for the synthesis of graphene oxide via oxidative chemical exfoliation have been elucidated. Special emphasis has been given on the use of graphene oxide as a carbocatalyst in organic synthesis.



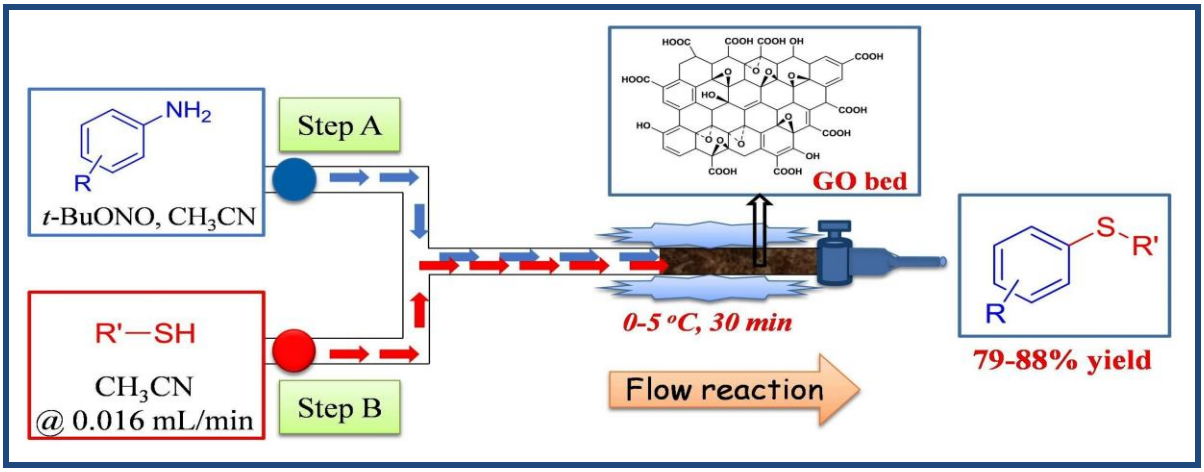
Graphene oxide catalyzed cross dehydrogenative coupling (CDC) between aromatic compounds and thiols have been presented in **Section B**. GO in combination with NaI has been used as the catalytic system for the regiospecific C–H sulfenylation of 1*H*-indole, 2-naphthol, resorcinol and 2-naphthylamines. A green strategy devoid of any transition metal and strong oxidants has been developed. Moreover, the use of thiols in place of other sulfenylation reagent makes the overall protocol atom-economic and environmentally benign. The heterogeneous nature of GO facilitates its easy reusability without any significant loss in its catalytic activity.



In **Section C** amine functionalized graphene oxide nanosheets (AFGONs) has been prepared by using a facile amine coupling reaction between GO and (3-aminopropyl)triethoxysilane. The nanocomposite has been used as a bifunctional catalyst for the selective formation of functionalized 1,4-dihydropyridines (1,4-DHPs), acridinediones and polyhydroquinolines. It has been presumed that a cooperative effect between the acidic and basic functionalities present in AFGONs might have exerted high catalytic efficiency as well as prevented over oxidation of the pyridine derivatives. A plausible mechanism has been proposed on the basis of control experiments. The reactions can be scaled up conveniently and the catalyst could be recycled for five consecutive runs without loss in its activity.

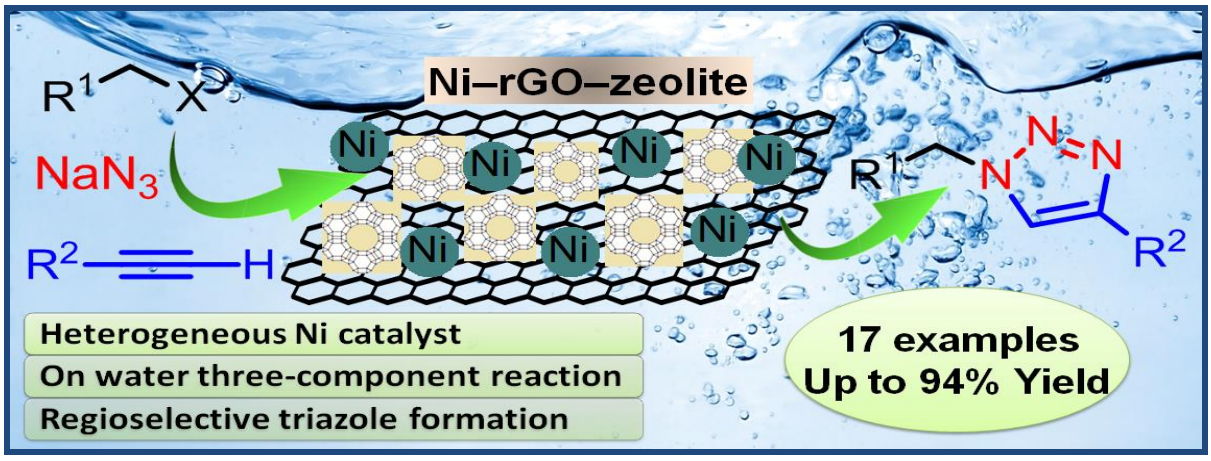


In **Section D** graphene oxide has been used as a carbocatalyst in Stadler-Ziegler reaction under continuous flow mode. The flow reactor is a relatively newer technology and constitutes a new paradigm for molecular assembly. In this section a sustainable continuous-flow protocol for the conversion of aryl amines to unsymmetrical thioethers has been described. This reaction undergoes through a two-step process involving graphene oxide catalyzed diazotization followed by sulfenylation with aryl/alkyl thiols. The GO catalytic bed has been found to be recyclable for ten consecutive runs without significant loss in its performance.



Chapter II has been divided into three sections. **Section A** presents a brief overview about the design and development of transition metal decorated graphene-based nanocomposites. The most common supports for anchorage of metal/metal oxide NPs include polymer blended graphene, graphene-zeolite and graphene-silica. Further applications of these nanocomposites as catalyst in synthetic organic chemistry has also been illustrated.

The synthesis and characterization of a new ternary nanocomposite (Ni–rGO–zeolite) based on reduced graphene oxide, zeolite Y and nickel NPs has been presented in **Section B**. The nanocomposite has been found to be an excellent catalyst for the regioselective synthesis of 1,2,3-triazoles in aqueous media. This is the first example of a heterogeneous nickel catalyzed alkyne azide cycloaddition (NiAAC). Moreover, the nanocomposite catalyst could be reused for four runs without loss in its activity.



Section C represents the synthesis of another ternary nanocomposite material (Cu@GO–SiO_2) from graphene oxide, silica and copper NPs. The spectroscopic and microscopic characterization of the nanocomposite revealed the presence of copper species in different oxidation states. This resulted in the exceptional catalytic activity of this nanocomposite towards different cross-coupling reactions like C–S, C–C, C–O and C–N.