ABSTRACT

Graphene, one-atom thick two-dimensional planar sheet of carbon, is the most promising materials in nanotechnology. Due to its huge specific surface area, high conductivity and charge mobility, excellent mechanical, thermal and electrical properties, it has been regarded as an important material for catalytic support and functional composite materials with unprecedented characteristics for developing a variety of catalysts. The main focus of this thesis is to synthesize and characterize the graphene and different functionalized graphene based nanocomposites and to study their catalytic properties. The work in the thesis is organized in six chapters. The chapter wise summarize is briefly explained below:

Chapter 1: Introduction

This chapter deals with general introduction on graphene and functionalized graphene based nanocomposites. The synthetic routes relevant to catalysis are discussed briefly with the latest literature review. After presenting an overview of the common and effective preparation methods, the catalytic applications of graphene and functionalized graphene based nanocomposites for organic transformations, energy related systems, photocatalysis and environmental protection are discussed. At the end of this chapter, the objective and the plan of the research are stated.

Chapter 2: This chapter discusses the synthesis and characterization of copper oxide nanoparticles decorated on reduced graphene oxide and its catalytic applications towards reduction of 4-nitrophenol and methanol electro-oxidation. This chapter is subdivided into two sections.

Section A describes a facile and novel hydrothermal method of preparing copper oxide supported on reduced graphene oxide (CuO-rGO) nanocomposites and their catalytic activity towards reduction of 4-nitrophenol (4-NP). The nanocomposites were prepared from mixture of GO and cuprous chloride (CuCl), where simultaneous formation of CuO and reduction of GO takes place without using any foreign materials. The synthesized composites were characterized by fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscope (SEM), and energy dispersive X-

ray(EDX). 4-NP was used as a model reaction to assess the catalytic activities of the prepared CuO-rGO nanocomposites. The nanocomposites exhibited excellent and stable catalytic activity towards reduction of 4-NP to 4-aminophenol (4-AP) in the presence of $NaBH_4$. The catalytic activities of the nanocomposites were also studied by changing the ratio of GO and Cu. The reaction kinetics followed pseudo-first-order rate law and the maximum value of the rate constant is 13.951 min^{-1}, which is superior to all other reported works. The catalyst can be easily regenerated and reused with good recyclability even upto five catalytic cycles.

Section B discusses the utilization of the CuO-rGO nanocomposite as an electro-catalyst for methanol electro-oxidation**.** The synthetic method was slightly modified where the nanocomposite was calcined at 400 °C. After calcinations at 400 °C, the nanocomposite ($CuO\text{-}rGO_{calcined}$) showed higher catalytic activity towards methanol electro-oxidation. The calcined composites were also characterized by using FTIR, XRD, Raman spectroscopy, SEM, EDX and dynamic light scattering (DLS) method. The electrochemical analyses of the compounds were evaluated by cyclic voltammetry (CV). In alkaline medium the $CuO\text{-}rGO_{calcined}$ nanocomposite undergoes irreversible methanol oxidation. The nanocomposite exhibits less positive characteristics peak (0.72 V) than of CuO (0.75 V) in forward scan also, the onset potential for the nanocomposites is lower than that of the CuO revealing that the overpotential for methanol oxidation decreases at the nanocomposites. Moreover, the peak current density at the $CuO\text{-}rGO_{calcined}$ nanocomposite is 2.4 times higher than that of CuO, suggesting the superior electro-catalytic activity of the nanocomposite. Chronoamperometry study reveals the superior durability and good tolerance against the oxidizing intermediate of the nanocomposites. The stability of the nanocomposite was further investigated for 100 continuous cycles. $CuO\text{-}rGO_{calcined}$ nanocomposite featuring low-cost, high durability and low onset potential reveals a superior catalytic activity for methanol electro-oxidation.

Chapter 3: This chapter deals with the synthesis characterization and concurrent electrochemical energy storage and conversion characteristics of Ni nanoparticles supported on polypyrrole-reduced graphene oxide (Ni/PPy/rGO). Ni/PPy/rGO nanocomposite was synthesized by mixing its precursors PPy/rGO and $NiCl_2.6H_2O$, where Ni^{2+} was reduced to Ni at pH 10.5. The obtained nanocomposite is characterized using FTIR, XRD, Raman Spectroscopy, SEM, DLS, XPS and TEM methods. The electrochemical energy storage properties of the nanocomposite were investigated using CV, galvanostatic charge/discharge and electrochemical impedance spectroscopy tests. Electrochemical analysis revealed that Ni/PPy/rGO nanocomposite has high specific capacitance of 763.49 Fg^{-1} at 1.31 Ag^{-1} current density with capacity retention of 96.75% after 200 cycles. Ni/PPy/rGO nanocomposite is also used as electrode in methanol electro-oxidation. CV and chronoamperometry were carried out to study the electrochemical energy conversion properties of the composite towards methanol electro-oxidation. The anodic current density of the Ni/PPy/rGO nanocomposite was much higher than that of Ni/rGO and PPy/rGO. Moreover, the onset potential of Ni/PPy/rGO nanocomposite was much lower than that of Ni/rGO and PPy/rGO. The results showed that the Ni/PPy/rGO nanocomposite is electro-catalytically active and highly stable.

Chapter 4: This chapter illustrates the photocatalytic degradation of dye over monoclinic-zirconium oxide supported on sulfonated graphene (*m*-ZrO_2/SG) under visible light. *m*-ZrO_2 was synthesized and annealed at three different temperatures and were incorporated into rGO as well as SG. The synthesized nanocomposites were characterized by using several analytical and spectroscopic methods. Photo degradation of methyl violet (MV) dye was studied by using SG, *m*-ZrO_2/rGO annealed at different temperatures and *m*-ZrO_2/SG (annealed at 1200˚C). It was found that the incorporation of *m*-ZrO_2 into rGO and SG has increased its catalytic activity. The catalytic activity of *m*-ZrO_2 further increased with increasing annealing temperatures. Thus, *m*-ZrO_2/SG catalyst was observed to possess the highest catalytic efficiency amongst the other synthetic composites. The catalyst can be reused after washing with absolute alcohol and deionized water.

Chapter 5: This chapter deals with selective dye adsorption by pH modulation by amine functionalized reduced graphene oxide-carbon nanotube hybrid. Simultaneous functionalization, reduction and hybridization of GO in GO-MWCNT hybrid were carried out by *p*-phenylenediamine (rGO-CNT-PPD). The adsorption properties of the hybrid for selective removal of MV and methyl orange (MO) from their mixture were investigated under different experimental conditions. The adsorption was co-related with the effects of pH, contact time and temperature. By changing the pH of the solution we can modulate the selectivity of the hybrid. At pH 7.0, it can remove 99.5% MV selectively from the mixture, while at pH 3.0, it can remove MO selectively having 98%

removal efficiency. The maximum adsorption capacity (q_m) of the hybrid for MV and MO are 298mg/g and 294 mg/g respectively, at 298 K temperature which are higher than several previously reported q_m values. The kinetics data for both dyes can be well fitted with the pseudo-second-order kinetic model and the adsorption of both the dyes followed Langmuir adsorption isotherm. The adsorbent can be easily regenerated and reused and its activity remains same even after five adsorption-desorption cycles. rGO-CNT-PPD hybrid could be a promising adsorbent for selective removal of synthetic dyes from their mixture by pH modulation.

Chapter 6: This chapter summarizes the chapter wise concluding remarks, major finding and future aspect of the present work. Several functionalized graphene based nanocomposites have been successfully synthesized and they showed enhanced catalytic properties compared to their individual counterparts. These nanocomposites could open a new dimension towards further development of new catalytic system for a range of applications in the upcoming years.