Photocatalysis is one of the emerging technologies to address the energy and environmental issues, for example production of H_2 from water, conversion of CO_2 to useful chemicals, chemical conversion/synthesis of organic molecules and removal of pollutants from water under light illumination.[1] Among the various photo-catalysts, semiconductors like TiO_2 and ZnO have been studied extensively for various photocatalytic applications.[2,3] The major drawbacks associated with these materials is the high recombination rate of photo-excited species, inefficiency for utilization of solar energy and photocorrosion, in turn leading to destabilization of semiconductors under the conditions of light irradiation.[4-6] In order to address these issues, elemental doping in semiconductors, combining with sensitizers or other semiconductor/conductor materials are the most common strategies introduced in the last decade. In this context, combination with graphene, a carbon based two dimensional material with honeycomb like lattice carbon atoms, has attracted much attention as an effective way to reduce charge recombination in the photocatalyst.[7] Because of their high surface area along with suitable electrical and mechanical properties, the graphene based materials find potential applications in various fields including energy and environmental. However, as outlined below there are issues related to the synthesis and application of these graphene based multicomponent photocatalytic systems.

Statement of problem:

- ✓ The synthesis of photocatalyst and their assembly with graphene based material usually requires harsh reaction conditions i.e. high temperature and pressure, extreme pH and toxic solvents, which in turn lead to secondary pollution. So there is a need to develop eco-friendly methodologies for the preparation of these materials.
- ✓ Graphene based materials help in trapping photo-generated electrons from the semiconductor, thereby improving the activity and photostability of the catalyst. But, the efficacy of graphene-semiconductor photocatalyst depends upon their interfacial interaction, which in turn leads to better charge transfer. So, the challenge here is to facilitate an effective interfacial assembly of graphene and semiconductor.

- ✓ In order to utilize solar light, efforts are being made to make the photocatalyst visible-light active. The aim is to develop an environmentally friendly procedure to fabricate the catalyst containing suitable components for visible-light activity.

Approach: Taking biomineralization process as inspiration, wherein positively charged polyamine plays the key role in formation of biominerals like Diatom under physiological conditions, the approach herein is to design bio-inspired methods for fabricating nanostructure materials. These multicomponent systems are further studied for their photocatalytic applications in the degradation of organic contaminants like dyes and in chemical conversions.

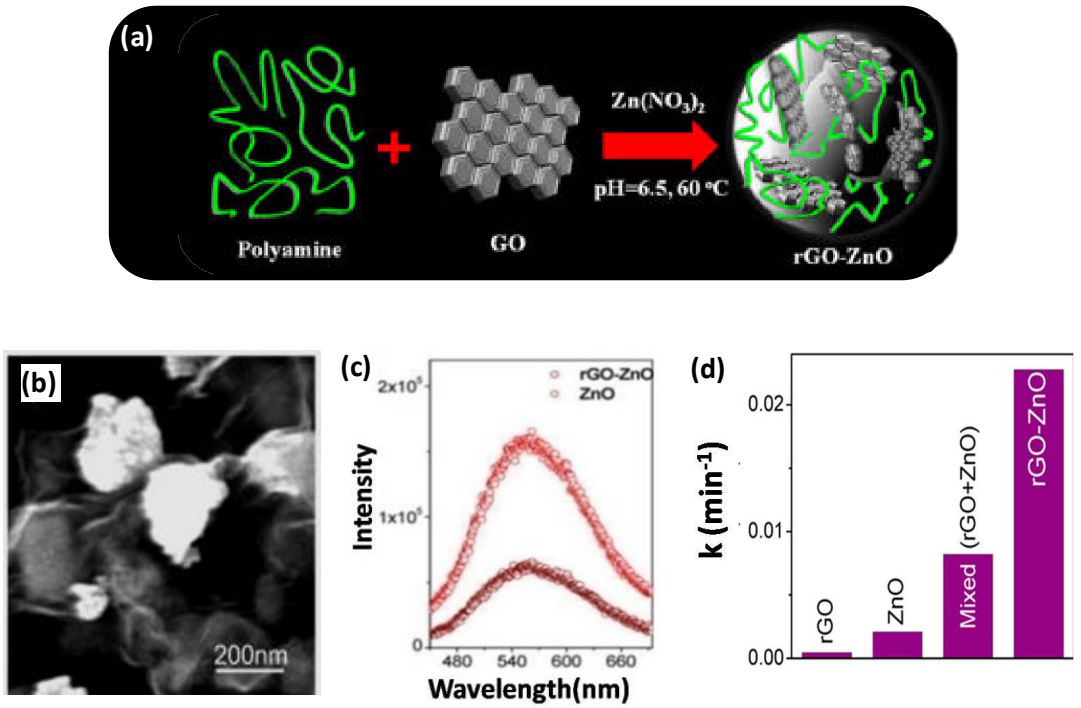

Figure 1: (a) Schematic representation of the polyamine-mediated mineralization of ZnO in presence of GO resulting in rGO-ZnO; (b) FE-SEM image of rGO-ZnO; (c) Luminescence spectra of rGO-ZnO and ZnO keeping the ZnO amount constant (Excited at 350 nm); and (d) Catalytic activity (k = apparent rate constant) of various catalysts in the RhB degradation under UV light irradiation.

In one of the approach, interfacial assembly of rGO (reduced Graphene Oxide) with ZnO is achieved in a single step using poly(allylamine), which simultaneously aids in the mineralization of ZnO nanostructures from zinc nitrate, reduction of graphene oxide

(GO), and finally their assembly to form rGO-ZnO under environmentally benign conditions (Figure 1). The interspersed nanocomponents in the assembled heterostructure results in enhanced photocatalytic activity under UV light, indicating an effective charge separation of the excited electrons. Furthermore, the composite structure provides stability against photocorrosion for recyclability of the catalyst.

In the next attempt, to make the photocatalyst visible-light active, Ag nanoparticles are introduced in rGO-ZnO system via sonochemistry to form rGO-ZnO-Ag. The photocatalytic activity and the photostability of the synthesized rGO-ZnO-Ag for dye-degradation under visible-light are evaluated (Figure 2).

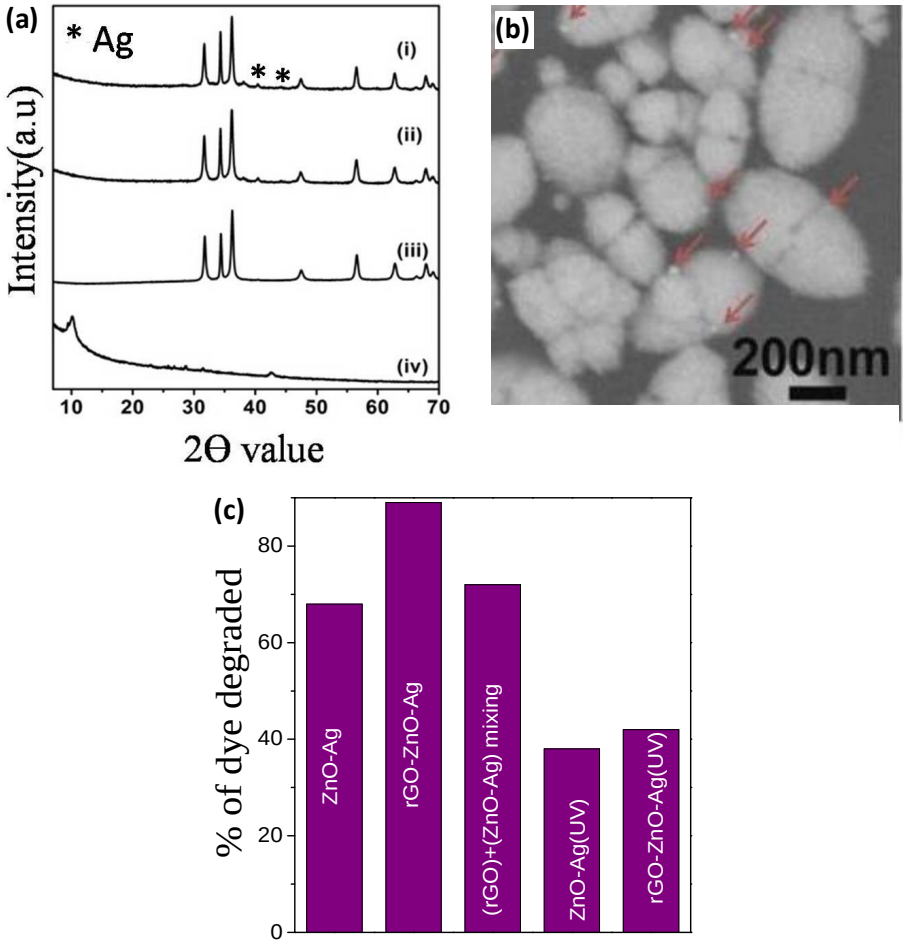

Figure 2: (a) XRD patterns of as-synthesized samples (i) rGO-ZnO-Ag, (ii) ZnO-Ag, (iii) ZnO and (iv) GO; (b) FE-SEM image of rGO-ZnO-Ag (The arrows indicate Ag nanoparticles); (c) catalytic activity of various catalysts in methylene blue degradation under visible-light irradiation.

Ag/AgCl is a well-known visible-light active photosystem, but the photoreduction of Ag^{+} during photocatalytic reactions is a major concern, which lowers the catalytic activity. So to improve their photostability, herein attempt is made to integrate the catalyst with GO sheets using poly(allylamine) hydrocholoride, which acts simulateneously as source of chloride ions for AgCl formation,an reducing agent to geretare Ag^{0} nanoparticle, and their assembly with GO. As examined, the GO-Ag/AgCl exhibits ~5 times higher photocatalytic activity and better photostability than Ag/AgCl (Figure 3).

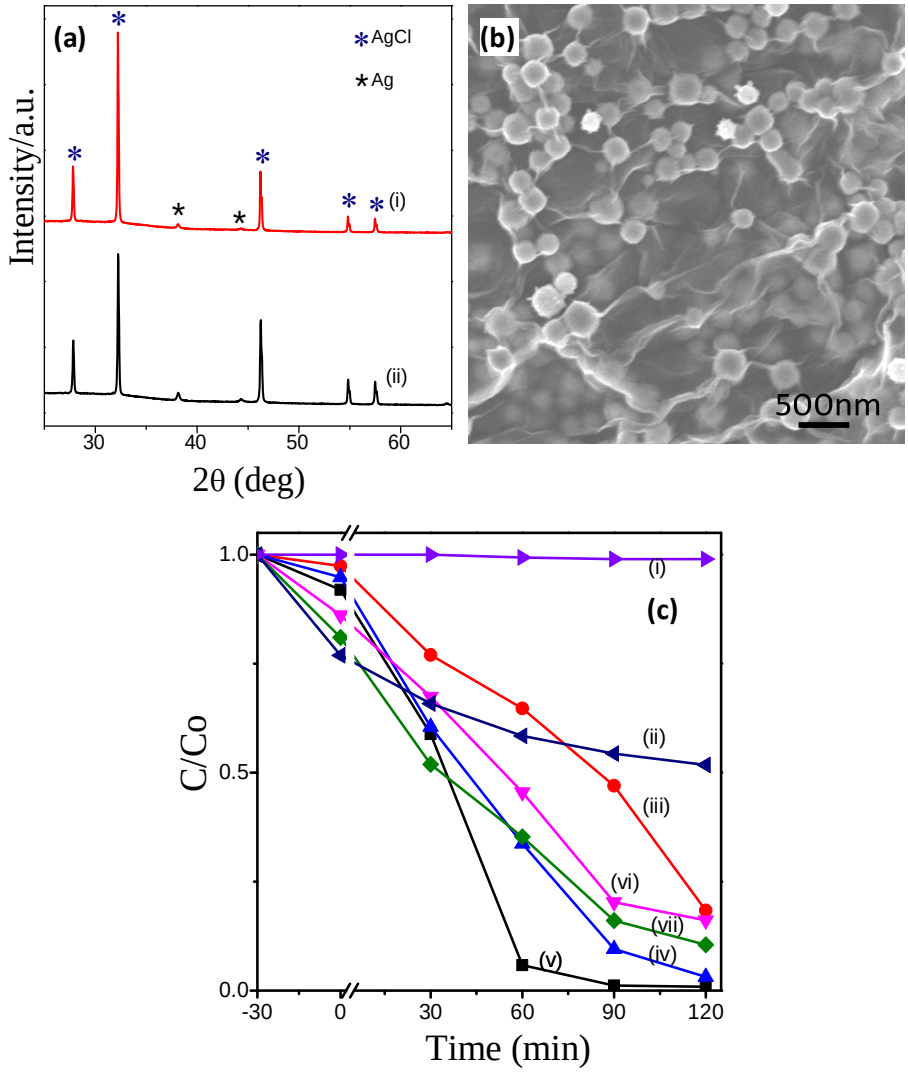

Figure 3: (a) XRD of the as-synthesized samples (i) Ag/AgCl and (ii) GO-Ag/AgCl; (b) FE-SEM image of GO-Ag/AgCl; and (c) Photocatalytic activity in the degradation of rhodamine B under visible-light irradiation for: (i) blank, (ii) GO, (iii) Ag/AgCl, and (iv-vii) GO-Ag/AgCl with varied GO amount (1.52, 4.16, 8.10 and 15.3 wt.%, respectively).

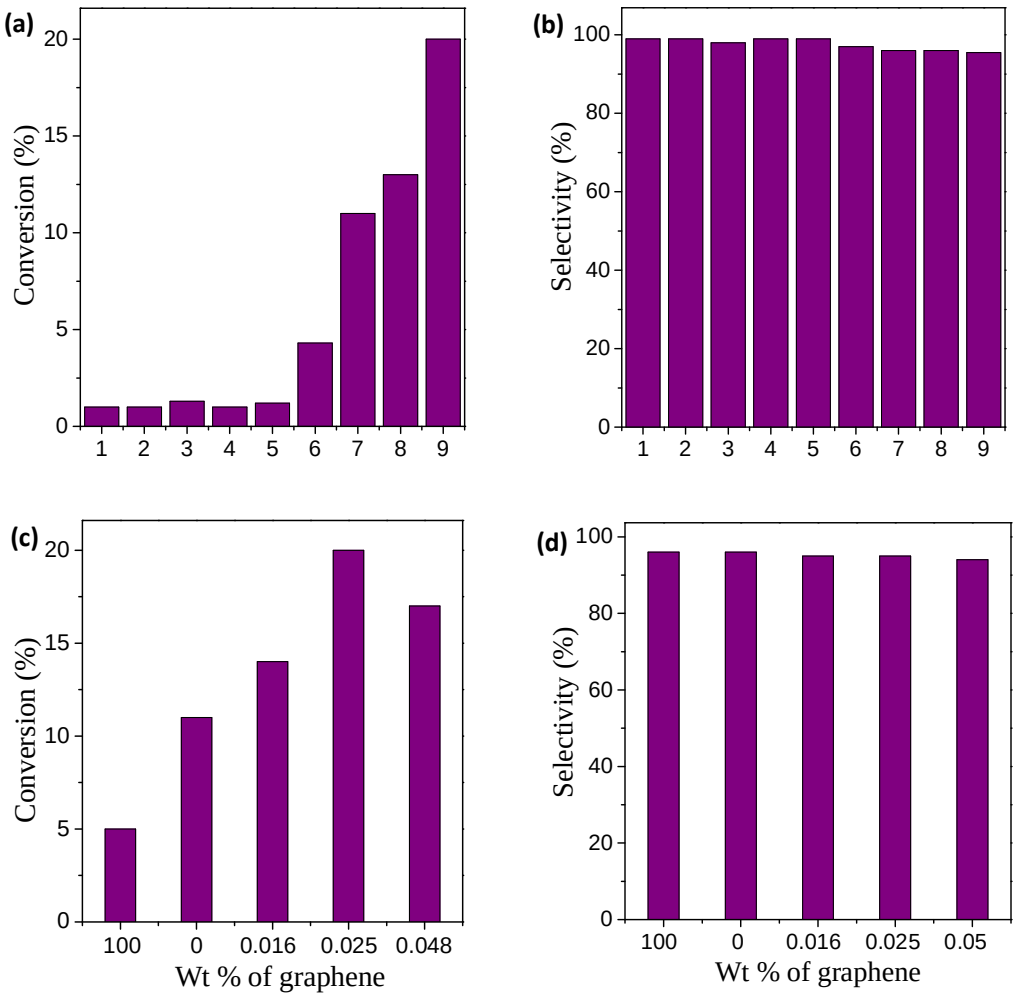

Figure 4: Photocatalytic activity in oxidation of benzyl alcohol under visible-light irradiation: (a) Conversion of benzyl alcohol, (b) Selectivity toward benzaldehyde obtained under various conditions: In absence of (1) any catalyst, (2) TEMPO, (3) AR (alizarin red), (4) light irradiation, and (5) O_2; Using (6) rGO-AR, (7) TiO_2-AR, (8) physical mixture of rGO and TiO_2 sensitized with AR dye, (9) rGO-TiO_2-AR as catalysts in presence of TEMPO, O_2 and visible-light irradiation. Effect of rGO content: (c) Catalytic activity and (d) Selectivity toward benzaldehyde with variation in the rGO content in rGO-TiO_2-AR catalytic system.

In an alternative approach, as discussed in this chapter, effective integration of rGO-TiO_2 with a photosensitizer (dye) to enable visible-light photocatalysis for chemical conversion is attempted. Sulpho rhodamine (SRhB) dye is used as the photosensitizer for the assembled rGO-TiO_2 system assembled with poly(allylamine). The photo-excitation of

the system is due to the excitation of dye under visible-light irradiation and then separation of the excited electron and hole via interaction with rGO-TiO_2 to be utilized in the photocatalytic reaction. The hole oxidises the TEMPO, which in turn oxidises benzyl alcohol and then the cycle continues to regenerate TEMPO. A systematic investigation on the effect of amount of rGO present in the catalyst shows that the presence of an optimum amount of polyamine-functionalized rGO in the catalyst improves the catalytic activity and selectivity towards aldehyde (Figure 4).

In summary, it is demonstrated that effective integration of graphene based materials with various photocatalysts is crucial. The use of polyamines not only provides an environmentally friendly synthesis route, but also allows suitable interfacial interactions to address issues related to activity and stability of the catalyst. Therefore the bio-inspired method is believed to further aid in developing other photocatalytic systems.