المعهد البترولي
THE PETROLEUM INSTITUTE
University & Research Center جامعة ومركز أبحاث

CHEMICAL ENGINEERING

Nanostructured Composites of Graphene/Metal Oxides for Effective Natural Gas Sweetening

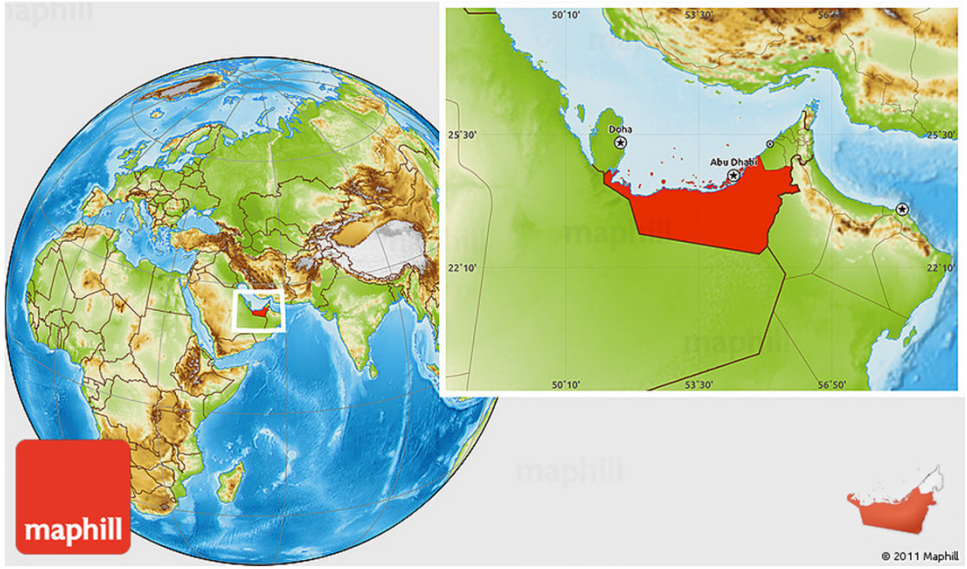


– Dr. Sunil Lonkar
Department of Chemical Engineering
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PI at Glance

- ***PI was established in 2001 in Abu Dhabi, UAE***
- *A premier engineering education institute in Middle East, 2000 undergraduate and graduate students, over 200 faculty*
- *The PI's sponsors and affiliates include the Abu Dhabi National Oil Company (ADNOC) and four major international oil companies that include BP, Japan Oil Development Company, Shell and Total.*





Outline

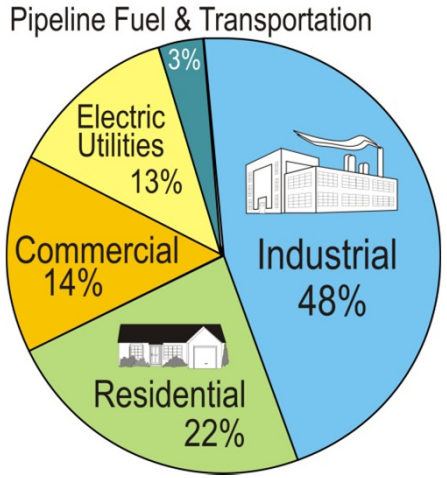
- *Introduction*
- *Synthesis and Characterization*

  - Graphene Oxide

  -Graphene/Metal Oxide nanohybrids
- *Adsorption Mechanism*
- *Sorption studies*
- *Remarks*

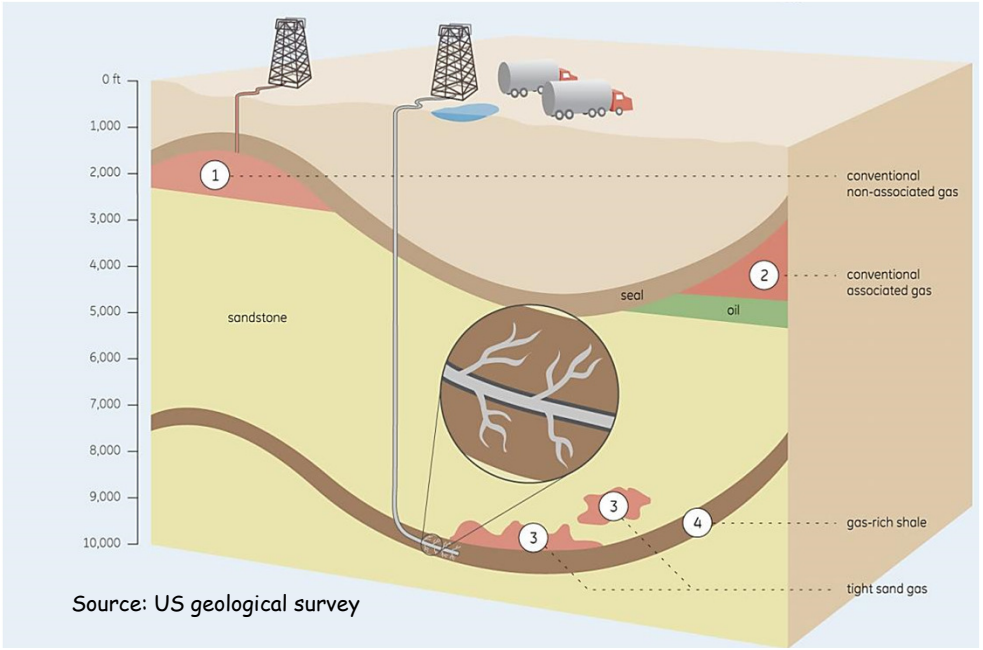
Introduction

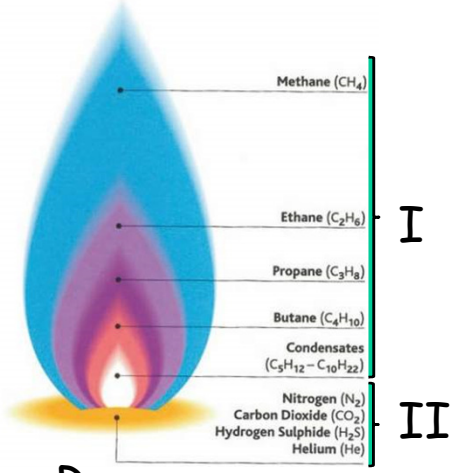
➢ Natural Gas (NG)



Cleanest fossil fuel

The geology of NG recourses





Raw gas

Purification

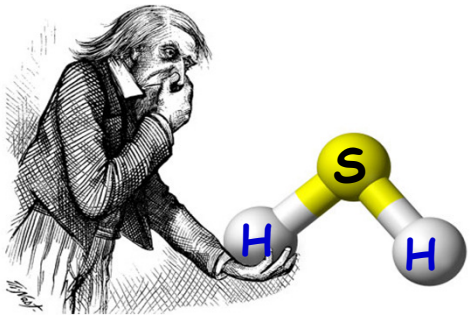


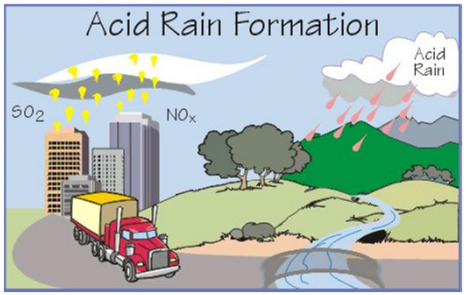
Purified gas

Natural Gas Sweetening

- ***Sour Gas***

- *The gas containing more than 4 ppm of hydrogen sulfide (H_2S) under STP*
- *Offensive odor*
- *High toxicity*
- *Serious corrosion problems*
- *Reduce efficiency of gas treatments*



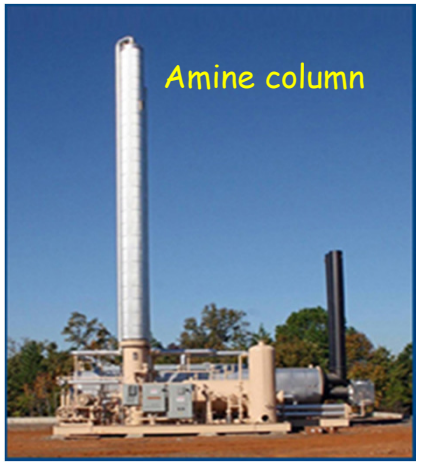


➢ ***Natural Gas sweetening processes***

Chemical absorption using aqueous amines (Amine Sweetening process)

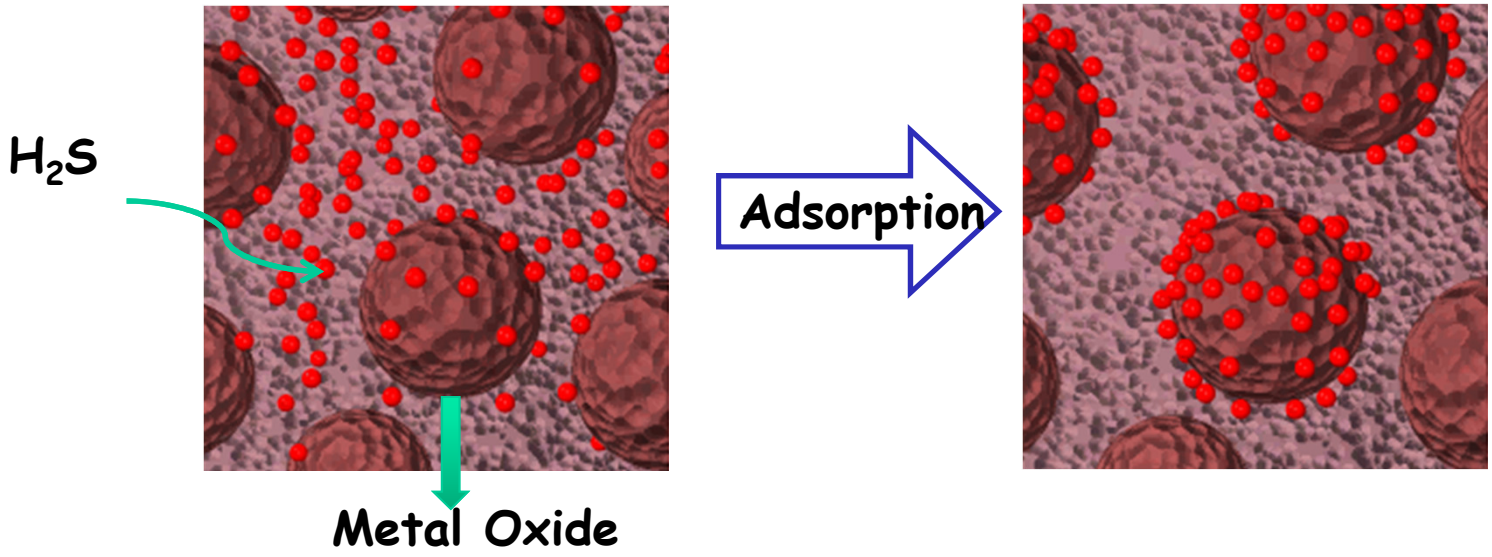
➢ **Challenges**

-Intensive energy requirement for regeneration
-Amine foaming in the absorber
-Corrosion
-Oxidative and thermal degradation of amine in the regenerator



Solid Adsorbents

- *Physical process: van der Waals and electrostatic forces*
- *High surface area, thermal stability, defined pore size and reactivity (polarity)*
- *Zeolites (natural and synthetic), Metal oxides, and Carbonaceous adsorbents for gas separations*



Hybrid Adsorbent Materials

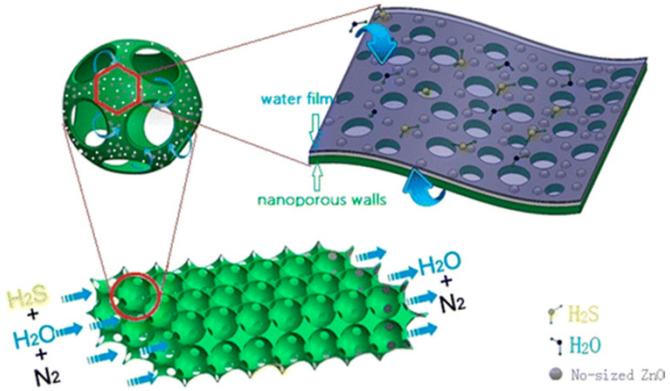
"Multidimensional hierarchical composites can take full advantages of each kind of components, which is an effective way for the preparation of multifunctional materials with exceptional properties"

- ***Metal Oxides:***

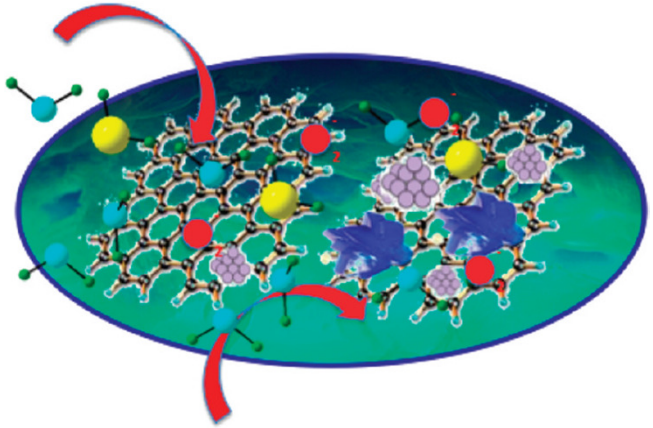
  -Zinc, Iron and Copper Oxides posses high thermal stability and proven reactivity towards H_2S

- ***Carbon materials***

  - Activated carbon, Graphene, CNTs etc. posses very high surface area, ability tailor surface properties



ZnO-silica composites with 3D macropores structures as sorbents for H_2S removal at RT, *Wang et al. ACS Appl. Mater. Interfaces*, Article ASAP



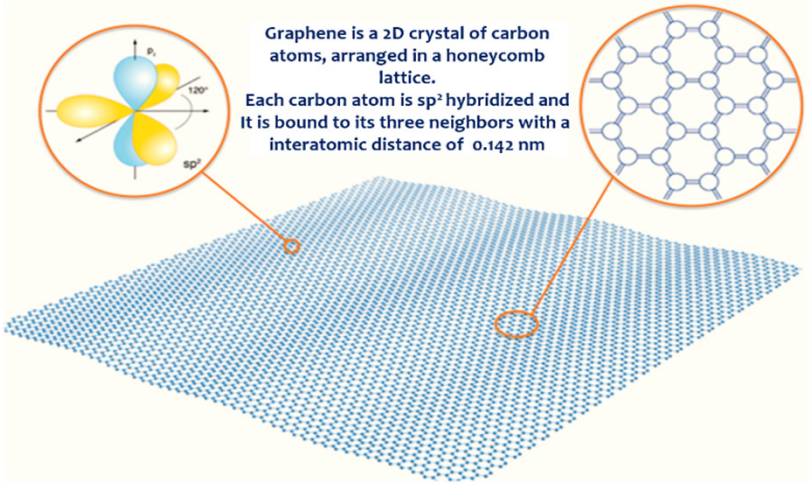
Graphite Oxide with Copper (Hydr) oxychlorides Bandosz et al., ACS Appl. Mater. Interfaces 2012, 4, 3316–3324

Chemosphere 58 (2005) 467–474., Chem. Engg. J. 166 (2011) 1032–1038.,.

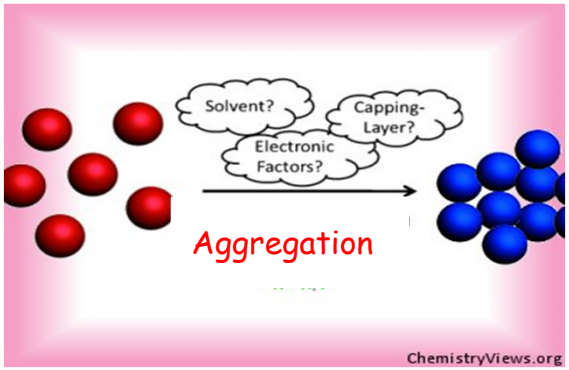
Graphene/Metal Oxide Nanohybrids

- ***Single layer of carbon atoms arranged in a honeycomb lattice***

- *Surface area = 2630 m^2/g ,*
- *Mechanical Properties (1200 GPa),*
- *Electrical Conductivity (3000 S/cm),*
- *Thermal conductivity (5000 W/(m.K)*

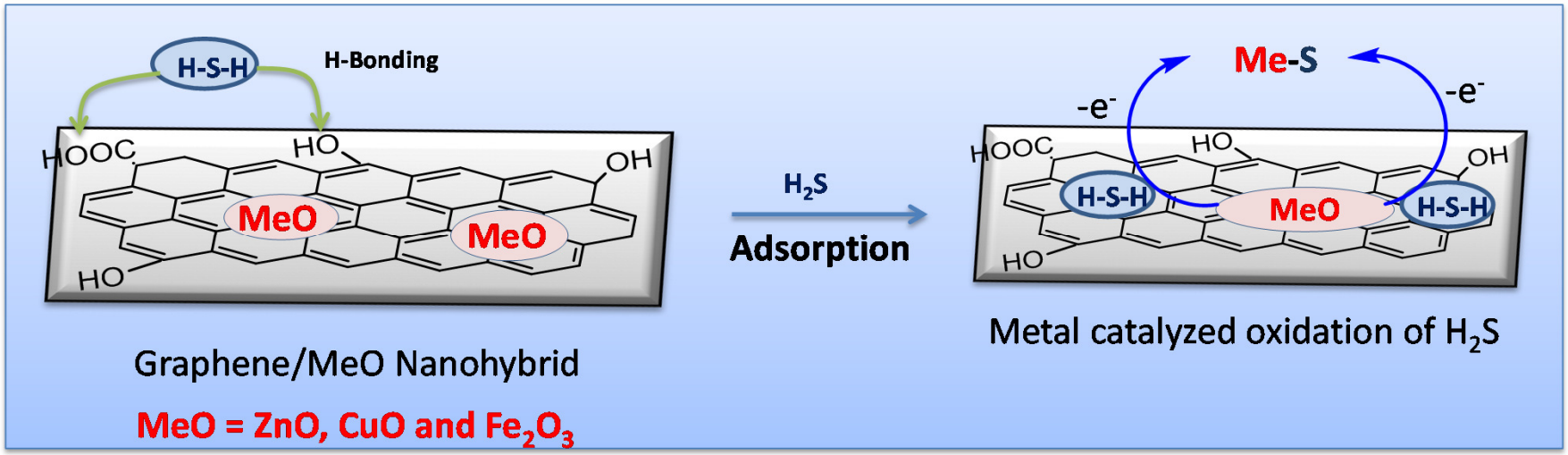


- Nanoparticle aggregation is major issue in gas-solid adsorption
- Loss in active surface area and subsequently lower efficiency as adsorbent.



- Hybridization of selected nanosized metal oxides (NMOs) supported on carbonaceous graphene. This combination allows for efficient adsorption due to the very high surface area of graphene and high reactivity of NMOs.

Adsorption mechanism



Hot air /O_2

I. $ZnO\ (s) + H_2S\ (g) \longrightarrow ZnS\ (s) + H_2O\ (g)$

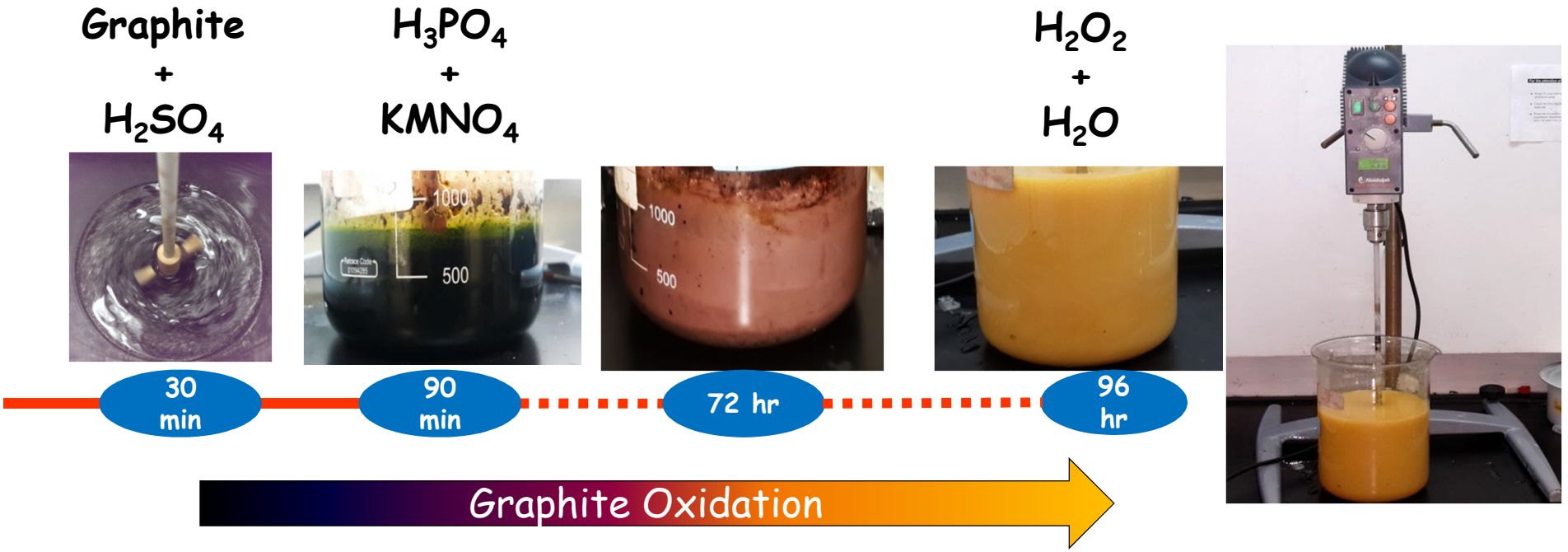
II. $CuO\ (s) + H_2S\ (g) \longrightarrow CuS\ (s) + H_2O\ (g)$

III. $F_2O_3\ (s) + 3H_2S\ (g) \longrightarrow Fe_2S_3\ (s) + 4H_2O\ (g)$

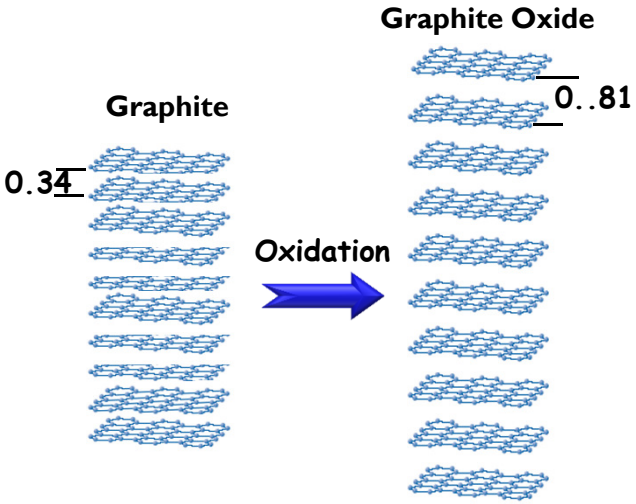
Experimental

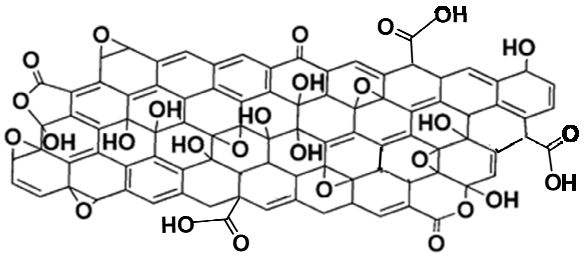
➢ GO synthesis (Improvised Tours Method)

- ✓ High surface area GO can be obtained
- ✓ May have high pore volume
- ✓ Greater amount of hydrophilic oxidized graphene
- ✓ More regular carbon framework and large GO sheets

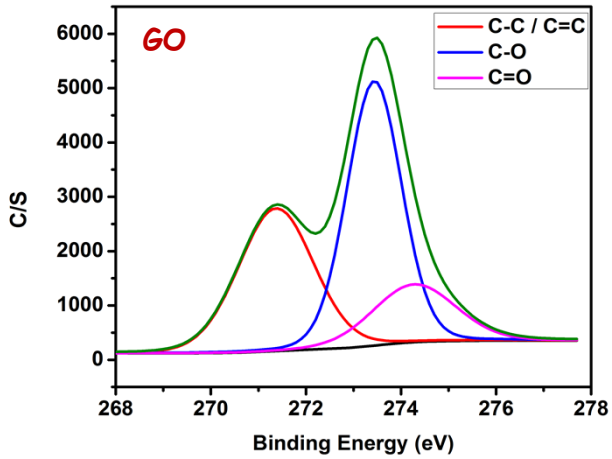


GO Characterization

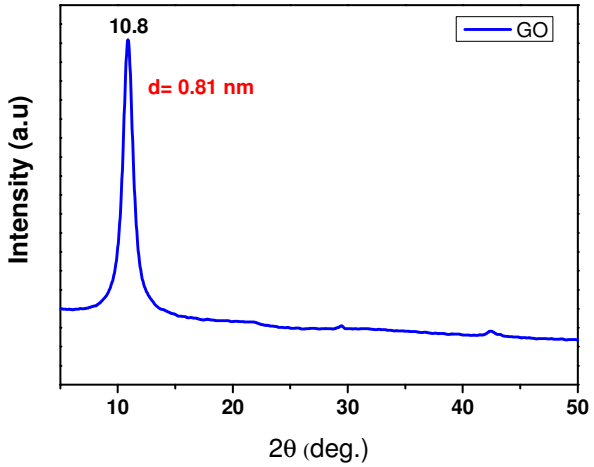




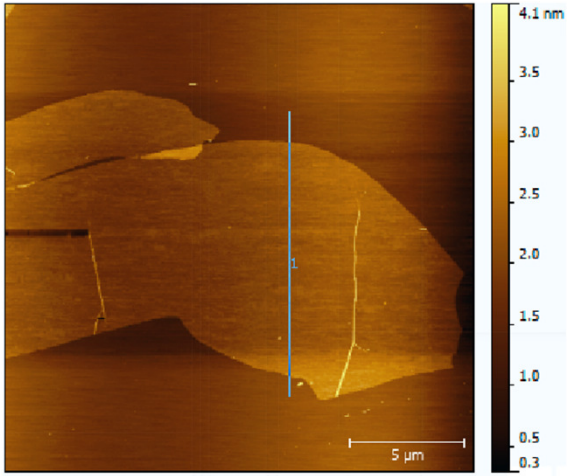
XPS



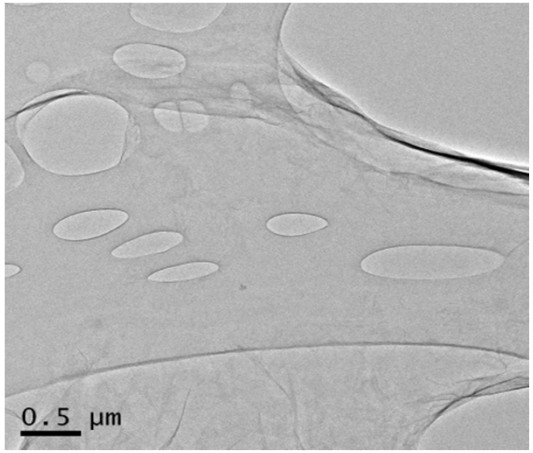
XRD



AFM

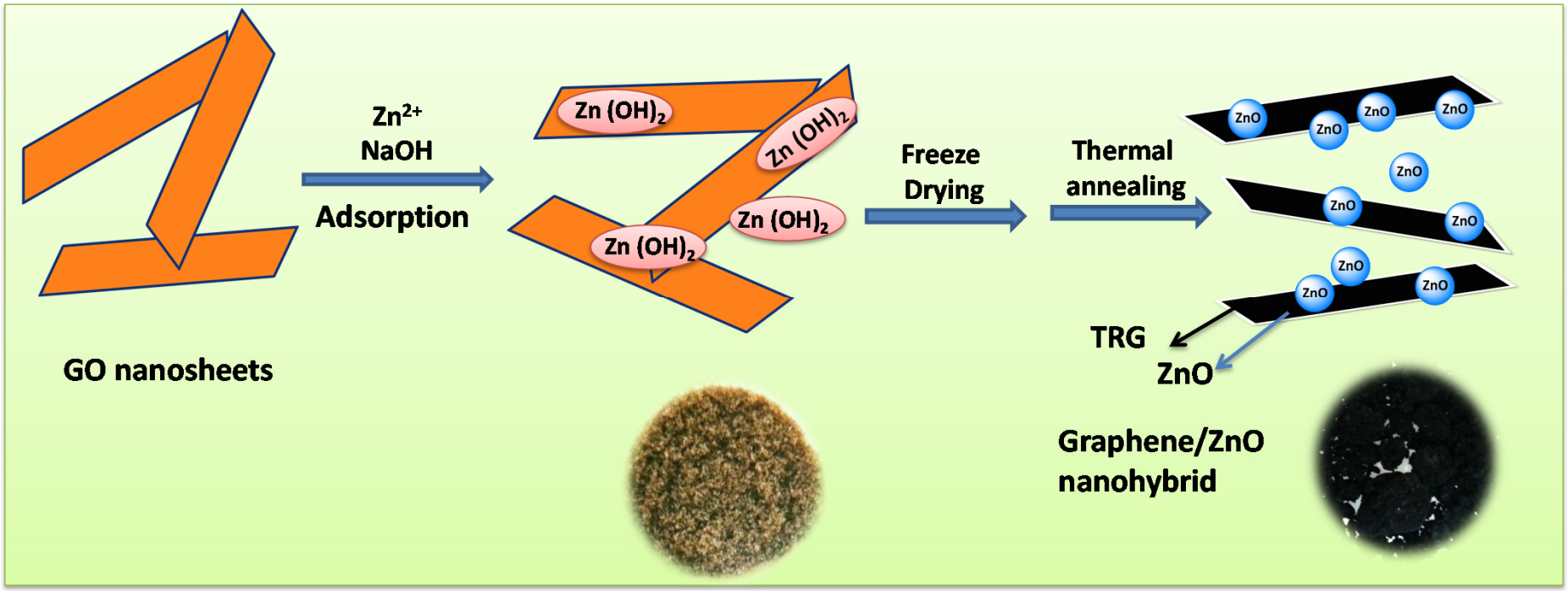


TEM



Synthesis of Graphene/Metal Oxide Hybrids

- In-situ thermo-annealed synthesis

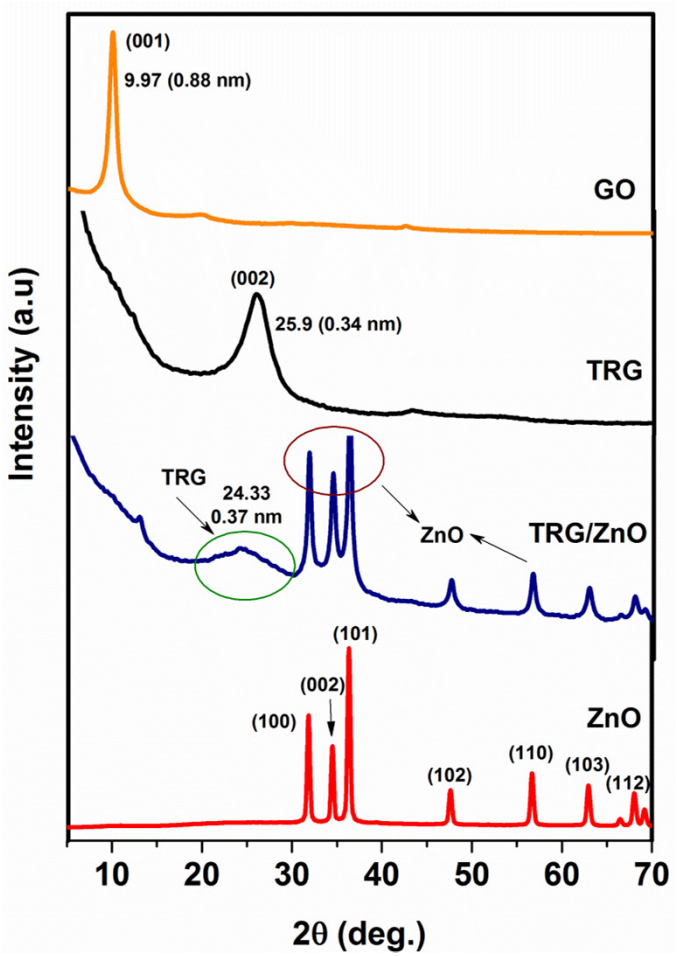


- Similar protocol was used to synthesize Graphene/CuO and Graphene/Fe2O3 composites

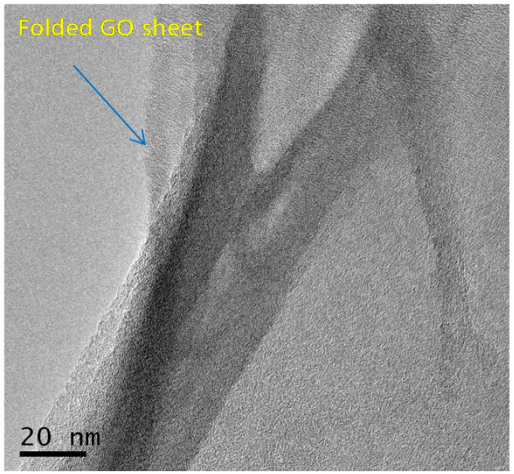
Characterization of Nanohybrids

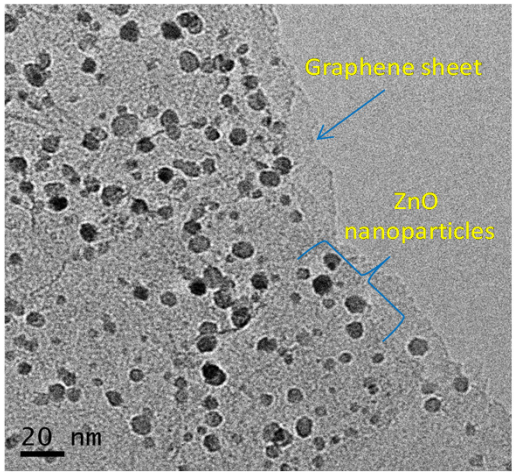
- ***Graphene/ZnO***

XRD



TEM

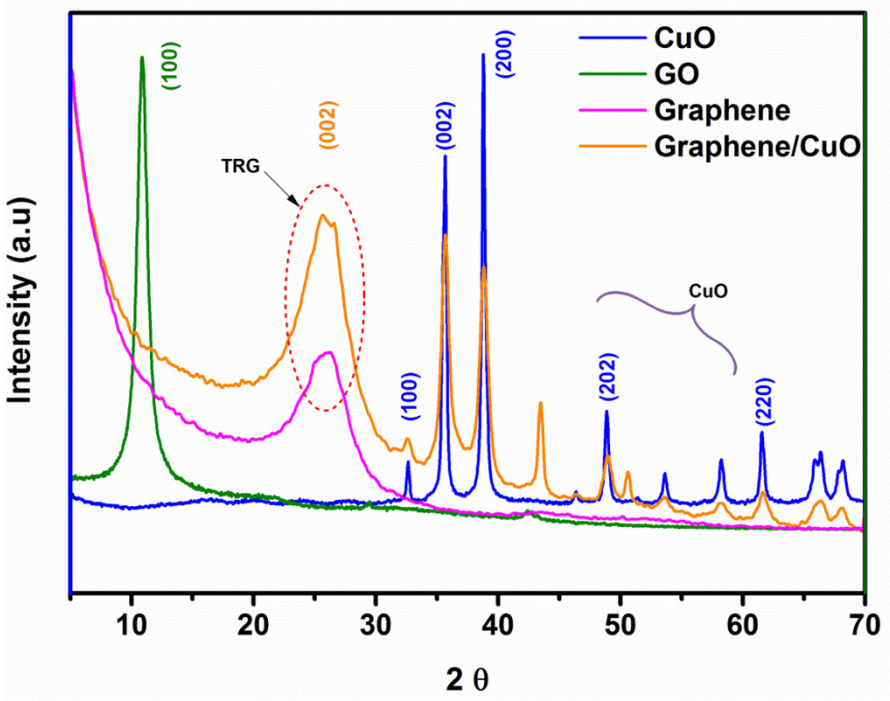




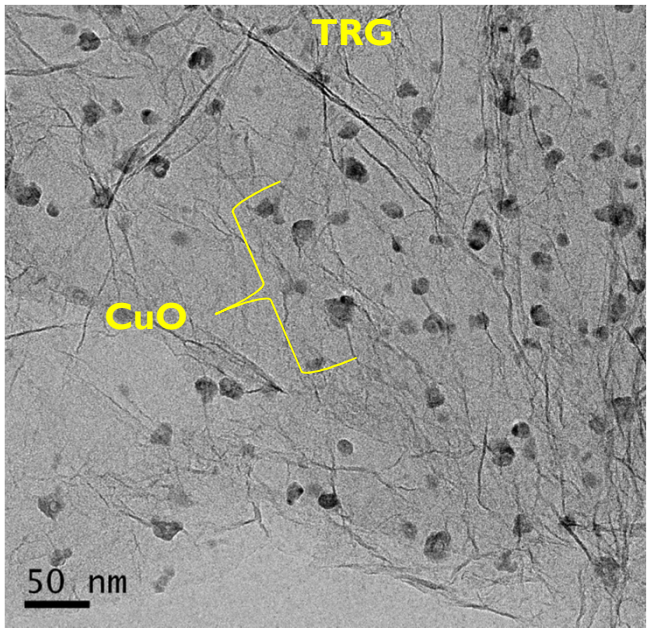
- XRD reveals formation of highly crystalline ZnO nanoparticles in conjunction with reduction GO to TRG
- TEM confirms the uniform dispersion of ZnO NPs into resulting hybrids.
- Particle size appear to be below 10 nm (ZnO QDs)

Graphene/CuO

XRD



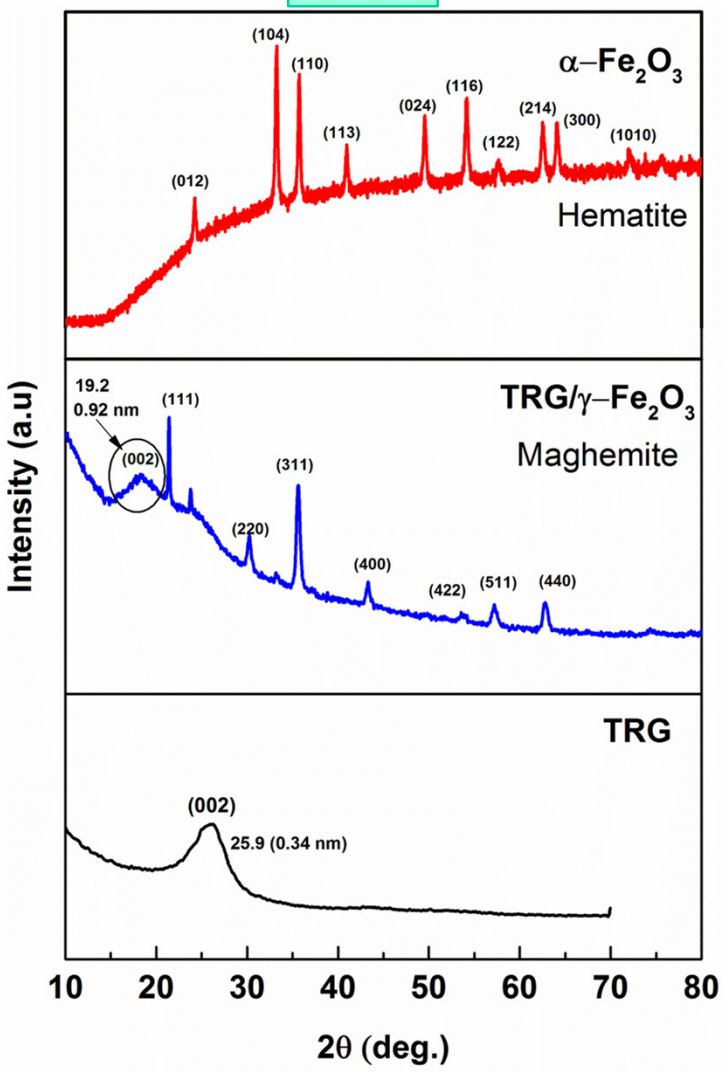
TEM



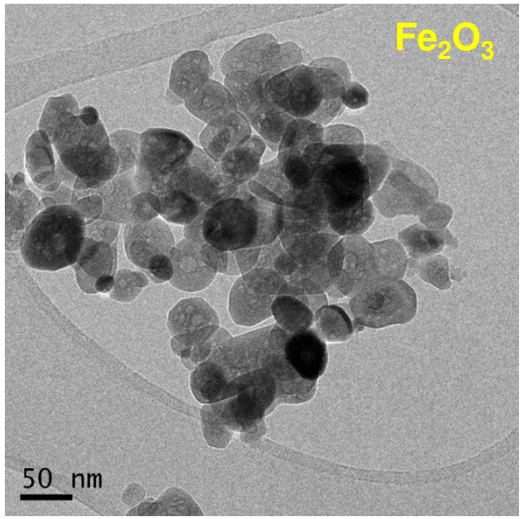
- XRD reveals formation of highly crystalline CuO nanoparticles in conjunction with reduction GO to TRG
- TEM confirms the uniform dispersion of CuO NPs into resulting hybrids having particle size below 20 nm

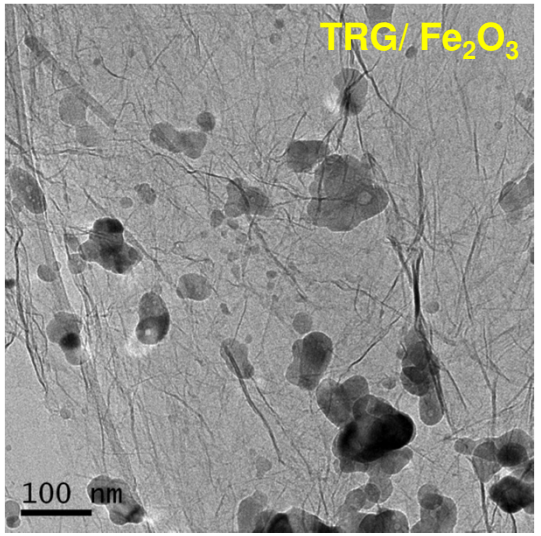
Graphene/Fe_2O_3

XRD



TEM





- XRD reveals formation of highly crystalline Fe_2O_3 nanoparticles in conjunction with reduction GO to TRG
- Phase change from alpha to gamma for Fe_2O_3 was observed in presence of graphene.
- Uniform dispersion of Fe_2O_3 NPs into resulting hybrids having particle size below 50 nm

H_2S sorption capacity

Adsorption Parameters:

Pressure = Ambient Pressure

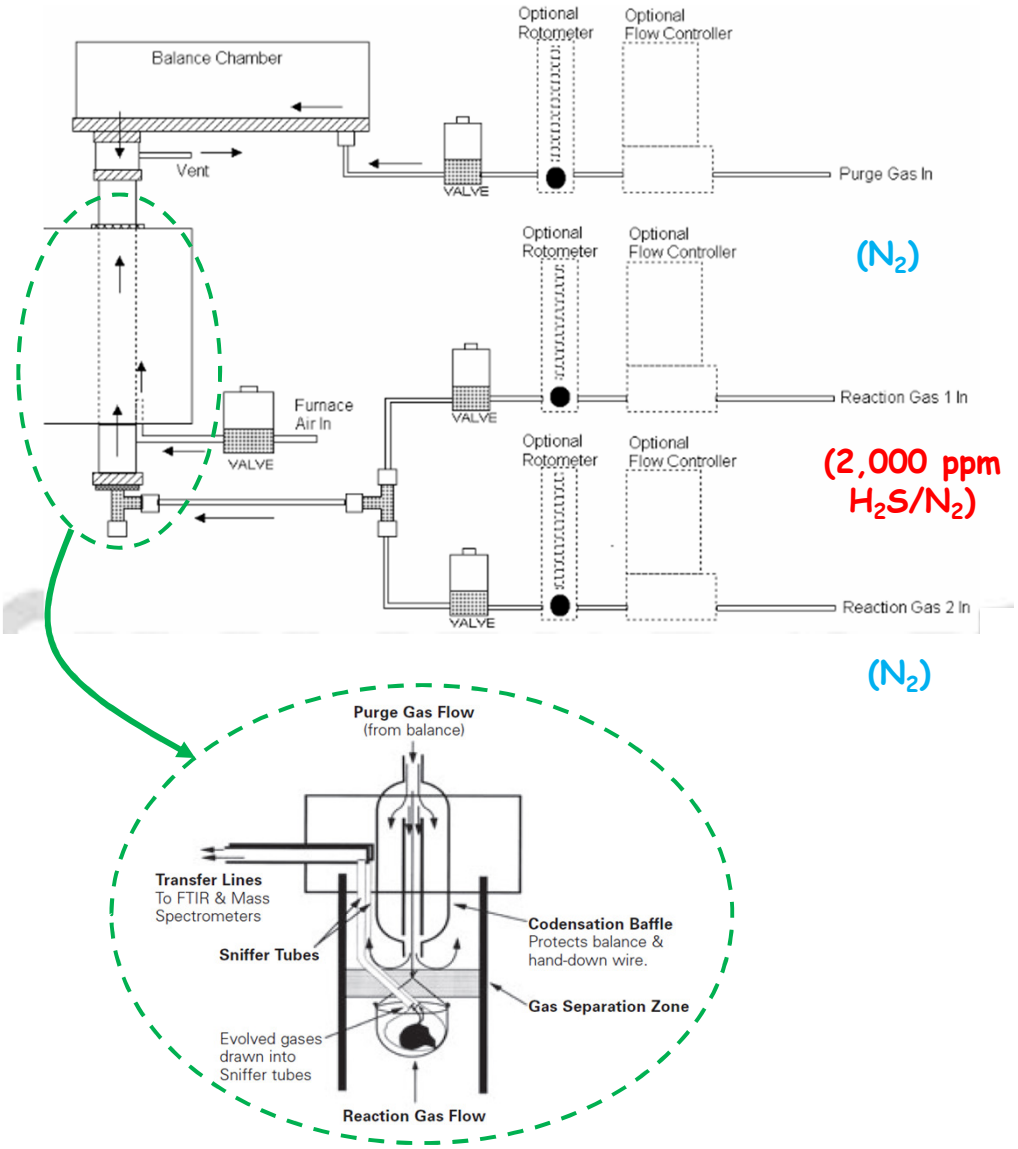
Temperature = 23-25°C

H_2S Flow Rate = 48 mL/min

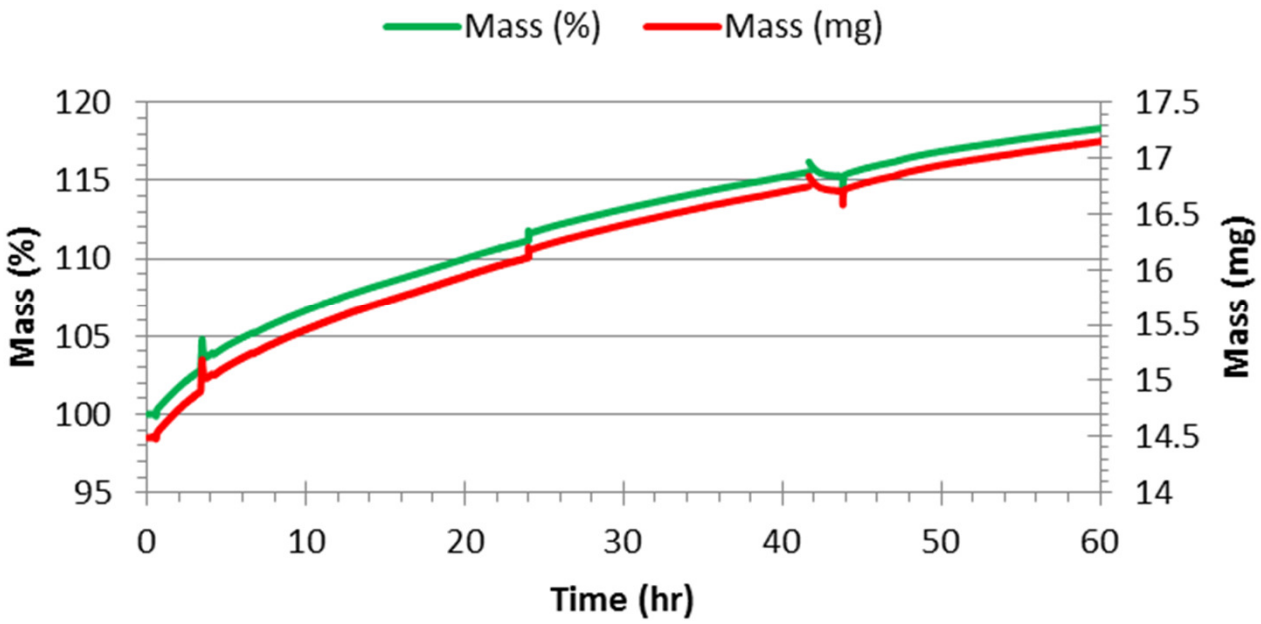
N_2 (Purge) Flow Rate = 50 mL/min

N_2 (Balance) Flow Rate = 20 mL/min





Graphene/ZnO H_2S Sorption capacity @ 25 °C



Sorbent = **TRG/ZnO (5 wt%)**

Mass Increase = 18% **(Maximum sorption capacity was NOT reached)**

Mass of H_2S Adsorbed (per 1.00 g sorbent) = 0.18 g H_2S

Moles of H_2S Adsorbed (per 1.00 g sorbent) = 5.28 mmol H_2S

Sorption Capacity of Sorbent = **5.28 mmol H_2S/g TRG-ZnO**

(Sorption capacity of Methyldiethanolamine [MDEA] is about **4.2 mmol H_2S/g amine)**

Remarks

- *Successfully synthesized nanohybrids of graphene with selected metal oxide (ZnO, CuO and Fe_2O_3).*
- *In-situ thermo annealing process is effective for NPs synthesis with simultaneous GO reduction.*
- *Characterization confirms that hybridization result in uniform dispersion of NPs on graphene surface.*
- *Initial H2S adsorption studies confirms that these hybrid posses great potential to be used in natural gas sweetening process*
- *Further studies are required to understand the regeneration process and efficiency of other metal oxides.*

Acknowledgements

- *Chair, Chemical Engineering Department*
- *Dr.Ahmed Abdala & Dr.Vikas Mittal*
- *Mr.Vishnu Pillai*

Thank you!!

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