

# WORK PERMIT

Department of Chemical and Biological Engineering

化學及生物工程學系

Project Title : Environmental Chemical Reactions on Carbon  
Nanomaterials

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Supervisor(s) : Prof. CM Chan

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Signature of Approval : liu



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**Name of researcher:** XIE, Wenjing

**Name of project supervisor:** Prof. Chi Ming Chan

**Date:** 2017-07-17

## 1. General Information

Name of Researcher: XIE, Wenjing

Name of Supervisor: Prof. Chi Ming Chan

Project Title: Environmental Chemical Reactions on Carbon Nanomaterials

Research Area: Nanomaterials, Environmental Chemical Reactions, Surface Analysis

Research Location: Room 7112

## 2. Project Description

In our daily life, sulfur dioxide ( $\text{SO}_2$ ) and nitrogen oxide (NO) emission from industry and vehicle are very serious to our health. It can be released to the atmosphere and oxidized by ozone or UV light in the air, then converted to sulfuric acid. The formed sulfuric acid will grow up slowly and finally become aerosols. These will lead to the formation of acid rain, haze or other air pollutions. Among these processes, the oxidation process is a key step. Up to now, studies about the mechanism of this process can be roughly divided into two opinions. The first one is related to pH modulation. In the equilibrium of sulfur dioxide and dissolved sulfur, the hydroxyl generated at the surface of sodium chloride can promote the conversion from sulfur dioxide to dissolved sulfur, thus make contribution to the formation of sulfate. As the rate of acid generation from the reaction of dissolved sulfur with ozone is equal to the rate of hydroxyl formation from the interface reaction, the pH will keep at nearly neutral. Therefore, the increased uptake of sulfur dioxide and the higher rate of sulfate formation in sea-salt particles will result in more rapid formation of sulfate in the marine boundary layer. Another theory stressed the importance of the oxidation intermediate formed in the process, which acts as a source of sulfuric acid. The reactions of alkenes with ozone are known to produce hydroxyl radical, the reaction between them led to the generation of oxidation intermediate, and then converted sulfur dioxide to sulfuric acid. But the real identity of oxidation intermediate still remains a question.

Carbon nanomaterials refer to a series of carbon allotrope, which sizes are less than 100 nm in at least one dimension. These kinds of materials usually include graphite, diamond, carbon nanotube, fullerene ( $\text{C}_{60}$ ,  $\text{C}_{70}$ ), graphene, graphyne.

Graphene consists of a flat monolayer of carbon atoms and has a two-dimensional (2D), honeycomb lattice structure. It can be wrapped up into 0D fullerene, rolled into 1D nanotube or stacked into 3D graphite. Thus, graphene can be seen as a basic unit of other carbon materials. Graphene has a delocalized pi bond, which enables free-moving electrons, thus displaying good conductivity. Fullerene consists of carbon atoms in the form of a hollow sphere. The most common types are C<sub>60</sub> and C<sub>70</sub>. Fullerene is very stable in room temperature and sparingly soluble in many solvents. Besides, using carbon nanomaterials for reaction is environmental friendly. Following these reasons, we choose these materials as reactant to generate radical and also treat it as a substrate to carry out the reaction.

Based on the above, this study focus on the conversion from SO<sub>2</sub> and NO to sulfuric acid and nitric acid and try to give a reasonable explanation.

### 3. Equipment List

- Analytical Balance, Miscellaneous Glassware, Flow cell, Pipette, Injector, Water Bath, Temperature Controller + Heater, Magnetic Stirrer, Centrifuge, Ultrasonic Cleaner, Vacuum Oven, UV Lamp, Ozone Generator, Spin Coater, pH indicator

### 4. Experimental Procedures

- Chemical reactions on carbon nanomaterials (Rm. 7112)

Graphite powder<sup>1-4</sup> (or graphene, C<sub>60</sub>, C<sub>70</sub>) will be reduced by sodium hydroxide<sup>5</sup> and ammonium chloride<sup>6</sup> solutions. Then the product will be oxidized by different oxidants, such as *meta*-chloroperoxybenzoic acid<sup>7</sup> (*m*-CPBA), potassium permanganate<sup>8</sup> and ammonium persulfate<sup>9</sup>. Dichloromethane<sup>10</sup> (CH<sub>2</sub>Cl<sub>2</sub>) was used as solvent. The reactions were carried out at room temperature (25 °C) by stirring the mixtures for different times. Different reaction temperatures will be tried. After the reaction, the products were washed with sodium carbonate<sup>11</sup>, CH<sub>2</sub>Cl<sub>2</sub> and methanol<sup>12</sup> then dried in oven. The residual solvents will be quenched by sodium thiosulfate<sup>13</sup>. Different solvents (Chloroform, THF, hexane, hydrochloric acid *etc.*)<sup>14-17</sup> will be tried for the reaction. The reacted graphite powder will be labeled by TFA<sup>18</sup> or TFAA<sup>19</sup> for characterization. The graphite powder will also be dissolved in different solvents

(THF, acetone, methanol, ethanol, pyridine, propanol, butanol, chlorobutane, benzene, toluene, xylene, chlorobenzene, dichlorobenzene, cyclohexane, dioxane, ethyl acetate, acetonitrile, DMSO, DMF, DOP *etc.*)<sup>20-37</sup> to prepare solutions with different concentrations. The solution will be spin coated on Si wafer<sup>38</sup> (washed by sulfuric acid<sup>39</sup> and hydrogen peroxide<sup>40</sup>). After the reactions, the graphite powder will be washed, filtrated, annealed, ultra-sonicated dried for cleaning.

The reacted graphite powder will be loaded on the glass slide and put into the flow cell reactor. N<sub>2</sub> gas will be flowed into the reactor to expel the existence air. Ozone will be generated by UV lamp ( $\lambda=254$  nm) irradiation of air. Then, ozone will be bubbled into the reactor. Next, open the UV lamp to vertically irradiate the surface of graphite for several hours. Bubble SO<sub>2</sub><sup>41</sup> or NO (prepared by Cu<sup>42</sup> or sodium nitrite<sup>43</sup> and nitric acid<sup>44</sup>) and water vapor or humid air into the reactor continuously at a constant flow rate and keep the reaction going for several hours. The SO<sub>2</sub> and NO gases will be dried by calcium chloride<sup>45</sup> or calcium oxide<sup>46</sup>. Another reaction method is to put the graphite powder in glass bottle and then exposed to SO<sub>2</sub> or NO for different times. Water vapor or humid air will also flow into the reactor and repeat the experiment. Using the BF<sub>3</sub>/butanol<sup>47</sup> method, standard compounds (4-hydroxy-3-methoxybenzaldehyde, 3,4-dimethoxybenzaldehyde, 1,2-dihydroxybenzene, 4-hydroxy-3-methoxybenzoic acid<sup>48-51</sup>) in aqueous phase will be used. A total volume of 0.25 mL of 10% BF<sub>3</sub>/butanol will be added to the sample. Hexane will be used to extract the derivatives. Then anhydrous Na<sub>2</sub>SO<sub>4</sub><sup>52</sup> and NaHCO<sub>3</sub><sup>53</sup> will be used to dry the samples. The exhaust will be connected to fume hood. After the reaction, take out the samples to characterize. Change graphite to graphene, C<sub>60</sub>, C<sub>70</sub> and repeat the procedures. The final product will be characterized by Raman, FTIR, SEM, TEM, AFM, TGA, NMR (Deuterated water, methanol, chloroform<sup>54-56</sup> will be used as solvents), Ellipsometry, Alpha-step, XPS and ToF-SIMS (These will be done in MCPF).



## 5. Procedure Template

PROCEDURE TEMPLATE					
Experimental	Experimental Procedure	Scale	Location	Method	
Procedure No.	Description	(Mass/Volume)	(Fumehood,bencctop,etc)	New or Existing	
1	Reduction of carbon materials	10-20 mg	Rm. 7112, Fume hood	Existing	
2	Oxidation of carbon materials under different times	10-20 mg	Rm. 7112, Fume hood	Existing	
3	Carbon materials disperse in different solvents	10-20 mg	Rm. 7112, Fume hood	Existing	
4	Wash, filtrate, anneal, ultrasonicate and dry the carbon materials	10-20 mg	Rm. 7112, Fume hood, Oven	Existing	
5	Carbon materials react with different gases	10-20 mg	Rm. 7112, Fume hood	Existing	
6	Prepare samples for characterization of different carbon materials	3-5 mg	Rm. 7112, MCPF	Existing	

## 6. Hazard and Operability Analysis (HAZOP)

HAZOP Template							
Hazard and Operability Analysis							
Activity:							
No.	Hazard	Hazard effect	Severity	Probability	Risk	Minimize risk by	Residual risk
1	Heat treatments will be conducted in high temperature.	Skin burn	L	M	M	Wearing gloves and avoiding touch with the heat source	L
2	Exposure to nanoparticles	Rapid uptake thru skin and epithelial cells, translocation along neurons	M	H	H	Wearing gloves, masks and conducting in the fume hood; minimizing the quantity of each experiment; avoiding to escape to the environment	M
3	Exposure to	Nanoparticles will rapid	H	H	H	Wearing gloves, masks	M



	nanoparticles and organic reagents Spillage of organic reagents	uptake thru skin and epithelial cells, translocation along neurons Organic reagents are flammable and harmful in case of exposure				and conducting in the fume hood; avoiding skin and eye contact; minimizing the quantity of each experiment; avoiding to escape to the environment; handling organic reagents gently; safely putting the waste into suitable waste containers	
4	Potential hazard of electric equipments	Skin burn or electric shock	L	L	L	Careful checking the equipments and wires before starting working	L
5	Potential hazard of electric equipments	Skin burn or electric shock	L	L	L	Careful checking the equipments and wires before starting working	L
<b>FINAL ASSESSMENT: Medium</b>							<b>Medium</b>

Remark: Severity–L=Low (Minor injuries, first aid); M=Medium (Hospitalization, medical leave); H=High (Serious injuries, fatality)

Probability–L=Low (Unlikely); M=Medium (Possible); H=High (Very Likely)

Note: Severity x Probability = Risk [eg. LxL=L; LxM=M; LxH=H; HxM=H; the product follows the higher severity or probability]

Higher Risk requires extensive risk minimization procedures



## 7. Operation Condition

Heat treatments: from room temperature to 1273.15 K or so in oven.

Dispersion process, including ultrasonic and magnetic stirrer: from room temperature up to 333.15 K or so.

## 8. Service List

Fume Hood

Compressed Air

Nitrogen Gas

Tap Water, Distilled Water, Deionized Water

Electrical Outlets: 220VAC, single phase, 13 Amp (max.)

## 9. Chemical List

No.	Material	State	Quantity per Experiments	MSDS attached
1	Graphene	solid	One piece	Yes
2	Graphite	powder	100 mg	Yes
3	C <sub>60</sub>	powder	5-10 mg	Yes
4	C <sub>70</sub>	powder	5-10 mg	Yes
5	Sodium hydroxide	powder	5-10 g	Yes
6	Ammonium chloride	powder	5-10 g	Yes
7	m-CPBA	powder	5-10 g	Yes
8	Potassium permanganate	powder	5-10 g	Yes
9	Ammonium persulfate	powder	5-10 g	Yes
10	Dichloromethane	liquid	100-200 mL	Yes
11	Sodium carbonate	powder	5-10 g	Yes
12	Methanol	liquid	10 mL	Yes
13	Sodium thiosulfate	powder	5-10 g	Yes
14	Chloroform	liquid	10 mL	Yes

15	THF	liquid	10 mL	Yes
16	Hexane	liquid	10 mL	Yes
17	Hydrochloric acid	liquid	10 mL	Yes
18	TFA	liquid	5 mL	Yes
19	TFAA	liquid	5 mL	Yes
20	Ethanol	liquid	10 mL	Yes
21	Acetone	liquid	10 mL	Yes
22	Ethyl acetate	liquid	10 mL	Yes
23	Benzene	liquid	10 mL	Yes
24	Toluene	liquid	10 mL	Yes
25	Xylene	liquid	10 mL	Yes
26	Chlorobenzene	liquid	10 mL	Yes
27	Dichlorobenzene	liquid	10 mL	Yes
28	Cyclohexane	liquid	10 mL	Yes
29	Dioxane	liquid	10 mL	Yes
30	DMF	liquid	10 mL	Yes
31	DMSO	liquid	10 mL	Yes
32	Pyridine	liquid	10 mL	Yes
33	Propanol	liquid	10 mL	Yes
34	Butanol	liquid	10 mL	Yes
35	Chlorobutane	liquid	10 mL	Yes
36	Acetonitrile	liquid	10 mL	Yes
37	DOP	liquid	10 mL	Yes
38	Si wafer	solid	5-10 piece	Yes
39	Sulfuric acid	liquid	30 mL	Yes
40	Hydrogen peroxide	liquid	10 mL	Yes
41	Sulfur dioxide	gas	50 mL	Yes
42	Cu foil	solid	One piece	Yes
43	Sodium nitrite	powder	5-10 g	Yes
44	Nitric acid	liquid	10 mL	Yes
45	Calcium chloride	powder	5-10 g	Yes
46	Calcium oxide	powder	5-10 g	Yes
47	BF <sub>3</sub> /butanol	liquid	10 mL	Yes
48	4-hydroxy-3-methoxybenzaldehyde	liquid	10 mL	Yes

49	3,4-dimethoxybenzaldehyde	liquid	10 mL	Yes
50	1,2-dihydroxybenzene	liquid	10 mL	Yes
51	4-hydroxy-3-methoxybenzoic acid	liquid	10 mL	Yes
52	Sodium nitrate	powder	5-10 g	Yes
53	Sodium bicarbonate	powder	5-10 g	Yes
54	D-chloroform	liquid	5 mL	Yes
55	D-methanol	liquid	5 mL	Yes
56	D-H <sub>2</sub> O	liquid	5 mL	Yes

## 10. Hazard and Operability Analysis

For chemicals (Numbers match with part 6):

No.	Materials	Summary of Hazards	Storage	Incompatibilities
	Sodium hydroxide	Causes severe skin burns and eye damage, serious eye damage, damage to organs. Harmful to aquatic life.	Store only in original container. Store in an area without drain or sewer access. Store in a cool, dry, well-ventilated location.	Separated from food and feedstuffs, organics, oxidizing materials, strong acids and metals.
	Ammonium chloride	Acute toxicity, eye irritation, harmful if swallowed.	Store in cool place. Keep container tightly closed in a dry and well-ventilated place.	Strong acids, strong bases, strong oxidizing agents.
	m-CPBA	Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Slightly hazardous in case of skin contact (corrosive), of eye contact (corrosive)	Refrigerate. Keep container tightly closed. Keep container in a cool, well-ventilated area.	Separate from acids, alkalis, reducing agents and combustibles.
	Potassium permanganate	Causes severe skin burns	Store in a	Separated from

		and eye damage, serious eye damage, respiratory irritation. Harmful if swallowed. Causes damage to organs through prolonged or repeated exposure	well-ventilated place.	combustible substances, reducing agents and powdered metals.
	Ammonium persulfate	Harmful if swallowed. Causes skin irritation, allergic skin reaction, eye irritation, allergy or asthma symptoms or breathing difficulties if inhaled. Decomposes on heating.	Store locked up. Fresh solutions of this product should be prepared for the most effective use in electrophoresis. Storage of solutions at 2-8 °C will allow their use for up to 12 hours.	This produces toxic and corrosive fumes including ammonia, nitrogen oxides and sulfur oxides. If in solution, reacts violently with iron, powdered aluminium and silver salts.
0	Dichloromethane	Causes eye and skin irritation. Causes respiratory tract irritation. Harmful if swallowed. May be harmful if inhaled. May cause central nervous system effects.	Store in a tightly closed container. Store in a cool, dry, well-ventilated area away from incompatible substances.	Keep from contact with oxidizing materials.
1	Sodium carbonate	Irritating to the eyes. Prolonged contact may cause skin irritation. Prolonged contact may cause skin irritation.	Store in a cool dry area. Prolonged storage may cause product to cake from atmospheric	Away from acids.
2	Methanol	Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation.	Store in a segregated and approved area. Keep container in a cool, well-ventilated	Reactive with oxidizing agents, metals, acids.

		Slightly hazardous in case of skin contact (permeator).	area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame).	
3	Sodium thiosulfate	Risk of explosion on contact with oxidizing agents. Decomposes on heating. Cause eye irritation, skin irritation, irritation of the digestive tract, respiratory tract irritation.	Store in a cool, dry place. Store in a tightly closed container.	Strong oxidizing agents, acids, chlorates, permanganates, silver salts, mercury, metal nitrates, sodium nitrite and iodine.
4	Chloroform	Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Slightly hazardous in case of skin contact (permeator).	Keep container tightly closed. Keep container in a cool, well-ventilated area. Sensitive to light. Store in light-resistant containers.	Reactive with metals, alkalis. Light.
5	THF	Hazardous in case of skin contact (irritant), of eye contact (irritant). Slightly hazardous in case of skin contact (permeator), of ingestion, of inhalation.	Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame).	Reactive with oxidizing agents, acids, alkalis.
6	Hexane	Hazardous in case of skin contact (permeator), of ingestion, of inhalation. Slightly hazardous in case of skin contact (irritant),	Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for	Reactive with oxidizing agents.

		of eye contact (irritant).	use. Avoid all possible sources of ignition (spark or flame).	
7	Hydrochloric acid	Very hazardous in case of skin contact (corrosive, irritant, permeator), of eye contact (irritant, corrosive), of ingestion. Slightly hazardous in case of inhalation (lung sensitizer).	Keep container tightly closed. Keep container in a cool, well-ventilated area.	Highly reactive with metals. Reactive with oxidizing agents, organic materials, alkalis, water.
8	TFA	Causes severe skin burns and eye damage. May cause severe and permanent damage to the digestive tract.	Store in a cool, dry place. Keep container closed when not in use. Keep containers tightly closed. Store in metal containers.	Metals, oxidizing agents.
9	TFAA	Extremely hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion. Very hazardous in case of inhalation.	May corrode glass. Store in an appropriate container. Corrosive materials should be stored in a separate safety storage cabinet or room.	Extremely reactive or incompatible with moisture.
0	Ethanol	Flammable liquid and vapor. Can accumulate in confined spaces, causing toxicity and flammability hazard. Closed containers may explode in heat of fire.	Store in suitable, labeled containers, a cool, dry, well-ventilated area, out of direct sunlight, and away from heat, sparks and flame, or any combustible or incompatible materials. Protect from damage and inspect frequently for signs of damage and/or	May react violently or explosively, with oxidizing agents, acids, acid chlorides, acid anhydrides, alkali metals, acetyl chloride, bromide, fluoride.



			leaking. Keep tightly closed.	
1	Acetone	Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Slightly hazardous in case of skin contact (permeator).	Store in a segregated and approved area (flammables area). Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use.	Reactive with oxidizing agents, reducing agents, acids, alkalis. Keep away from direct sunlight and heat and avoid all possible sources of ignition (spark or flame).
2	Ethyl acetate	Hazardous in case of ingestion, of inhalation. Slightly hazardous in case of skin contact (irritant, permeator), of eye contact (irritant).	Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame).	Reactive with oxidizing agents, acids, alkalis. Moisture sensitive.
3	Benzene	Very hazardous in case of eye contact (irritant), of inhalation. Hazardous in case of skin contact (irritant, permeator), of ingestion.	Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame).	Highly reactive with oxidizing agents, acids.
4	Toluene	Flammable liquid and vapor. Danger of serious damage to health by prolonged exposure.	Keep containers tightly closed in a dry, cool and well-ventilated place. Flammables area. Keep away from heat and sources of ignition.	Strong oxidizing agents, Strong acids

5	Xylene	Hazardous in case of skin contact (irritant, permeator), of eye contact (irritant), of ingestion, of inhalation.	Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame).	Reactive with oxidizing agents, acids.
6	Chlorobenzene	Very hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Inflammation of the eye is characterized by redness, watering, and itching.	Store in a separate safety storage cabinet or room. Keep away from sources of ignition. Keep container tightly closed. Keep in a cool, well-ventilated place.	Keep away from heat.
7	Dichlorobenzene	Very hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion. Inflammation of the eye is characterized by redness, watering, and itching.	Keep away from sources of ignition. Keep container tightly closed. Keep in a cool, well-ventilated place. Keep container dry. Keep in a cool place.	Keep away from heat.
8	Cyclohexane	Slightly hazardous in case of skin contact (irritant, permeator), of eye contact (irritant), of ingestion, of inhalation.	Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame).	Reactive with oxidizing agents.
9	Dioxane	Hazardous in case of eye contact (irritant), of ingestion, of inhalation.	Keep container in a cool, well-ventilated area. Keep container	Reactive with oxidizing agents.

		Slightly hazardous in case of skin contact (irritant, permeator).	tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame).	
0	DMF	Hazardous in case of skin contact (irritant, permeator), of eye contact (irritant), of ingestion, of inhalation.	Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame).	Reactive with oxidizing agents, acids.
1	DMSO	Slightly hazardous in case of inhalation (lung irritant), skin contact (irritant, permeator), eye contact (irritant), or ingestion. Mutagenic for mammalian somatic cells and bacteria or yeast. Flammable in presence of open flames and sparks, of heat.	Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame). Hygroscopic. Sensitive to light. Store in light-resistant containers.	Oxidizing agents, reducing agents, acids, alkalis.
2	Pyridine	Hazardous in case of skin contact (irritant, permeator), of eye contact (irritant), of ingestion, of inhalation.	Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame).	Reactive with oxidizing agents, acids.
3	Propanol	Hazardous in case of skin	Keep container in a	Reactive with

		contact (irritant), of eye contact (irritant), of ingestion. Slightly hazardous in case of skin contact (sensitizer, permeator).	cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame).	oxidizing agents, acids, alkalis.
4	Butanol	Very hazardous in case of skin contact (irritant, permeator), of eye contact (irritant), of ingestion, of inhalation. Inflammation of the eye is characterized by redness, watering, and itching.	Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame).	Highly reactive with oxidizing agents, reducing agents. Slightly reactive to reactive with organic materials, acids, alkalis.
5	Chlorobutane	Very hazardous in case of eye contact (irritant), of ingestion, of inhalation. Inflammation of the eye is characterized by redness, watering, and itching.	Keep away from sources of ignition. Keep container tightly closed. Keep in a cool, well-ventilated place.	Keep away from heat.
6	Acetonitrile	Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Severe over-exposure can result in death.	Store in a segregated and approved area. Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use.	Avoid all possible sources of ignition (spark or flame).
7	DOP	Hazardous in case of eye contact (irritant), of inhalation (lung irritant).	Keep container dry. Keep in a cool place. Ground all equipment containing material.	Highly reactive with oxidizing agents, acids.

			Carcinogenic, teratogenic or mutagenic materials should be stored in a separate locked safety storage cabinet or room.	
9	Sulfuric acid	Very hazardous in case of skin contact (corrosive, irritant, permeator), of eye contact (irritant, corrosive), of ingestion, of inhalation. Skin contact may produce burns.	Hygroscopic. Reacts. Violently with water. Keep container tightly closed. Keep container in a cool, well-ventilated area.	Reactive with oxidizing agents, reducing agents, combustible materials, organic materials, metals, acids, alkalis, moisture.
0	Hydrogen peroxide	Prolonged contact can cause moderate to severe irritation. Hydrogen peroxide solutions of 20% to less than 35% are corrosive to eyes based on animal information.	Store in a cool, well-ventilated area, out of direct sunlight, away from heat and ignition sources and away from combustible materials.	Slightly reactive to reactive with reducing agents, combustible materials, organic materials, metals, acids, alkalis.
3	Sodium nitrite	Very hazardous in case of eye contact (irritant), of ingestion, of inhalation. Hazardous in case of skin contact (irritant). Slightly hazardous in case of skin contact (permeator). Prolonged exposure may result in skin burns and ulcerations.	Oxidizer. Hygroscopic. Air sensitive. Keep container tightly closed. Keep container in a cool, well-ventilated area.	Separate from acids, alkalies, reducing agents and combustibles.
4	Nitric acid	Very hazardous in case of skin contact (corrosive,	Keep container tightly closed. Keep container	Separate from acids, alkalies, reducing

		irritant, permeator), of eye contact (irritant, corrosive), of ingestion. Slightly hazardous in case of inhalation (lung sensitizer).	in a cool, well-ventilated area.	agents and combustibles.
5	Calcium chloride	Inhalation of dust may cause irritation to the respiratory organs. Solid calcium chloride might cause mild skin irritation (dry skin).	Store in a tightly closed container in cool, dry and ventilated area. Protect against mechanical damage.	Methyl vinyl ether, water, zinc, bromine trifluoride, mixtures of lime and boric acid, barium chloride, and 2-furan percarboxylic acid.
6	Calcium oxide	Very hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Hazardous in case of skin contact (corrosive, permeator), of eye contact (corrosive).	Keep container tightly closed. Keep container in a cool, well-ventilated area.	Reactive with organic materials, acids, moisture.
7	BF <sub>3</sub> /butanol	Harmful if swallowed. Very toxic by inhalation. Vapors may cause drowsiness and dizziness. Causes severe burns.	Keep container closed.	Keep away from heat, sparks, and open flame.
8	4-hydroxy-3-methoxybenzaldehyde	Hazardous in case of eye contact (irritant), of ingestion, of inhalation.	Keep container tightly closed. Keep container in a cool, well-ventilated area. Moisture sensitive.	Sensitive to light. Store in light-resistant containers.
9	3,4-dimethoxybenzaldehyde	Very hazardous in case of eye contact (irritant). Inflammation of the eye is characterized by redness, watering, and itching.	Keep container dry. Keep in a cool place. Ground all equipment containing material. Keep container tightly closed. Keep in a cool,	Combustible materials should be stored away from extreme heat and

			well-ventilated place.	away from strong oxidizing agents.
0	1,2-dihydroxybenzene	Harmful if absorbed through the skin. May cause central nervous system depression. Harmful if swallowed. May cause methemoglobinemia. Causes eye and skin burns.	Keep container closed when not in use. Keep from contact with oxidizing materials. Store in a cool, dry area away from incompatible substances.	Away from strong oxidizing agents.
1	4-hydroxy-3-methoxybenzoic acid	Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation.	Keep container dry. Keep in a cool place. Ground all equipment containing material. Keep container tightly closed. Keep in a cool, well-ventilated place.	Combustible materials should be stored away from extreme heat and away from strong oxidizing agents.
2	Sodium nitrate	Hazardous in case of ingestion. Slightly hazardous in case of skin contact (irritant), of eye contact (irritant), of inhalation.	Keep container tightly closed. Keep container in a cool, well-ventilated area.	Separate from acids, alkalies, reducing agents and combustibles.
3	Sodium bicarbonate	Slightly hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation.	Keep container tightly closed. Keep container in a cool, well-ventilated area.	Away from acids.
4	D-chloroform	Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation.	Keep container tightly closed. Keep container in a cool, well-ventilated area. Store in light-resistant containers.	Reactive with metals, alkalis.
5	D-methanol	Hazardous in case of skin contact (irritant), of eye contact (irritant), of	Keep container in a cool, well-ventilated area. Keep container	Reactive with oxidizing agents, metals, acids.

		ingestion, of inhalation.	tightly closed and sealed until ready for use.	
6	D-H <sub>2</sub> O	Slightly hazardous in case of ingestion.	Keep container tightly closed. Keep container in a cool, well-ventilated area.	Keep away from heat.

**For gas, carbon materials and others:**

Hazard	Summary of Hazards	Store or Incompatibilities
Nanoparticles (graphene, graphite, C <sub>60</sub> , C <sub>70</sub> )	Rapid uptake thru skin and epithelial cells, translocation along neurons	Wearing gloves, masks and conducting in the fume hood; minimizing the quantity of each experiment; avoiding to escape to the environment.
Sulfur dioxide	Toxic if inhaled. Causes severe skin burns and eye damage. May explode if heated.	Keeping container in a well-ventilated place; avoiding breathing gas; wearing protective gloves/ protective clothing/ eye protection/ face protection.
Si wafer and Cu foil	Skin contact causes irritation.	Keep away all sources of ignition. Store in well-ventilated area. Avoid light.
Potential hazard of electric equipment	Skin burn or electric shock	Careful checking the equipment and wires before starting working.



## 11. Waste List

Waste Streams	Physical Form	Disposal	Volume /Mass	Frequency
Nanoparticles	solid	Dissolve in minimum quantity of an appropriate solvent	3-5 mg	once a week
Gases	gas	The exhaust will be expelled to fume hood	20-30 mL	once a day
Organic solvents	liquid	Non-halogenated organic solvents	10-30 mL	once a week
Inorganic acids	liquid	Dilute into diluted acids and dispose into acid disposal tanks	5-10 mL	twice a week
Inorganic salts	liquid	Dilute and dispose into corresponding disposal tanks	5-10 mL	twice a week
Si wafer	solid	Wash for reuse	3-5 piece	twice a week

## 12. Assessment of Significant Risks

### Chemicals

- SO<sub>2</sub> and NO are irritant gases. They can affect the eyes and respiratory systems and is hazardous at even low concentrations.
- C<sub>60</sub>, C<sub>70</sub>, graphene, graphite are easy to uptake thru skin and epithelial cells. Also, they may be inhaled into body.
- Organic solvents are flammable and harmful in case of direct skin exposure. Besides, incaution inhalation may cause potentially serious consequences

### Electrical Equipment Hazards

- Ensure fume hood is running properly and is regularly maintained.
- Avoid electric shock or wire wear and twining when using electronic machines.

- An independent ozone generator will continuously produce ozone.

### **13. Safety Precautions**

#### Safety Training Required

- Safety training courses, including chemical safety I & II organized by HSEO, should be attended.
- Some characterization techniques will be trained by technicians and faculties once they are needed during experiment.

#### Personal Protective Equipment

- Personal protective equipment including lab coat, safety goggles and nitrile protective gloves, masks will be worn when handling chemicals. Chemical contact with eyes, skin and clothes will be avoided.

#### Warning Sign Required

- Chemicals will be stored based on hazard categories with clear labeling. The date of receipt, use and expiration will be noted. The list of chemicals stored in the laboratory will be posted at convenient location. Chemical inventory will be minimized to reduce overall risks.

#### Fume Cupboard and Exhaust Point

- Fume cupboard must be used. Experiments should be done in the fume cupboard. Regularly maintenance is required.
- Ozone destructor and exhaust point will be double-checked to ensure ozone is destroyed and exhausted properly.
- The waste of sulfur dioxide must be connected to fume hood to ensure proper exhaust.

#### Fire Hazards

- For flammable materials, they will be kept away from source of ignition and heating.
- Experiments must be done in fume hood.

#### Electrical Hazards

- To prevent electrical shock, proper grounding will be installed.

#### Emergency Shut Down Procedures

- Stop hot plate, vacuum pump and syringe pump's power supply.
- Equipment training offered by technical staff is required.

## **14. Actions in case of Abnormal and Emergency Situations**

#### Service Failure

- For fume hood failure: Stop any experiment inside the fume hood immediately.
- For electricity failure: Stop heater, syringe pump, vacuum pump.
- For water supply failure: Stop the heater of heating under reflux set up.

#### Action in case of fire or explosion

- Activate the fire alarm by pressing the break-glass fire alarm button.
- Report the accident to Security Control Centre by dialing 8999.
- Alert other people. If SAFE to do so, try to put out the fire by using firefighting equipment.
- DO NOT take any personal risk. If the fire gets beyond your control, evacuate immediately by following the procedures below.
- Close the door of the room on fire.

#### Action in case of loss of containment or accidental spillage

- Alert co-workers
- If safe to do so,
  - Confine the spill with appropriate materials.
  - Turn off remotely all heat/ignition sources if flammable vapor is involved.
  - Ask for assistance if necessary.
- Ask for assistance if necessary.
- Press the Emergency Ventilation button (do not activate this button in case of fire).

- Inform the Security Control Centre by dialing 8999 from a safe location.
- Evacuate everyone in the affected area. Leave contaminated clothing and close the door.
- Activate local warning system to prevent others from entering the room.
- If possible, maintain a safe distance from the scene, keep the entrance or access routes in sight and help to prevent entry to the affected room.
- If conditions allow, remain to assist the emergency response team.