# WORK PERMIT

**Department of Chemical and Biological Engineering**

**化學及生物工程學系**

Project Title : Synthesis of Size-Controlled Cu2O Catalyst for Electrochemical Reduction of CO2.

Researcher(s) : Xuyun GUO

Supervisor(s) : Prof. Minhua SHAO

Work Plan No. : 17049

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Signature of Approval :

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HONG KONG UNIVERSITY OF SCIENCE AND TECHNOLOGY DEPARTMENT OF CHEMICAL AND BIOMOLECULAR ENGINEERING

# Synthesis of Size-Controlled Cu2O Catalyst for Electrochemical Reduction of CO2

## Work Plan: 17049

Researcher: Dr. Guo Xuyun

Supervisor: Dr. Shao Minhua

7/12/2017

## 1. General Information

| | |
|---|---|
| Name of Researcher: | Dr. Guo Xuyun |
| Name of Project Supervisors: | Dr. Shao Minhua |
| Project Title: | Synthesis of Size-Controlled $Cu_2O$ Catalyst for Electrochemical Reduction of $CO_2$ |
| Research Area: | Chemical Engineering |
| Location: | Lab 7102 |
| Proposed Start Date: | Aug. 2017 |

## 2. Experiment/Project Description

### Objective:

The aims and the objectives of this project are:
a.) to synthesize the $Cu_2O$ nanoparticle catalysts with different sizes;
b.) to test the $CO_2$ reduction performance of the $Cu_2O$ nanoparticle electrocatalyst.

Experiment Description:

$Cu_2O$ nanoparticle catalysts with different sizes will be synthesized by electrochemical deposition. Cu salts are the main salt and K salts are using as the supporting electrolyte. The electrochemical catalytic performance was tested with using $CO_2$ saturated $KHCO_3$ aqueous solution.

# 3. Equipment List

| Equipment | Location |
|---|---|
| Electronic balance | 7101, 7102 |
| Sample bottle | 7102 |
| Ultrasonic instrument | 7102 |
| Oven | 7102, 7102SC |
| Electrochemical workstation | 7102 |
| Beakers (of various volumes), pipette | 7102 |
| X-ray diffraction (XRD) equipment | 2150 |
| X-ray photoelectron spectroscopy (XPS) | 2149 |
| Transmission electron microscope (TEM) – JEM-2010F | 2218 |
| Scanning electron microscope (SEM) – JSM-7100F | 1125 |
| Gas chromatography (GC) | 7102 |

# 4. Experimental Procedures

### 4.1 Synthesis of size-controlled $Cu_2O$ nanocatalysts

(4.1.1) 1 mmol $Cu(NO_3)_2$[(1)] and 0.1 M $KNO_3$[(2)] are dissolved into 100 mL water for deposition electrolyte;
(4.1.2) Copper foam is cleaned by 1 M HCl solution for 20 s[(3)], following rinsed by DI water;
(4.1.3) 7 mL deposition electrolyte is adding into the electrochemical cell;
(4.1.4) Copper foam is used as working electrode, while Pt as counter electrode and Ag/AgCl as reference electrode, applied potential was adding through electrochemical work station;
(4.1.5) After the electrodeposition, the electrode is rinse by DI water and dried by $N_2$.

### 4.2 Electrocatalytic Performance Test

(4.2.1) 0.1 M $KHCO_3$[(4)] are dissolved into 200 mL water for electrolyte;
(4.2.2) 60 mL electrolyte is adding into the H type electrochemical cell, purged $CO_2$[(5)] continually for $CO_2$ saturation.
(4.2.3) As-fabricated $Cu_2O$/Copper foam is used as working electrode, while Pt mesh as counter electrode and Ag/AgCl as reference electrode, applied potential was adding through electrochemical work station;
(4.2.4) The generated gases are purged into GC every ~20 min for testing the gaseous product.

### 4.3 Sample Characterization

*Transmission Electron Microscope(TEM)*

The TEM images of a typical sample are obtained on a JEM-2010F microscope;

*Scan Electron Microscope(SEM)*

The SEM images of the as-fabricated $Cu_2O$ before and after $CO_2$ reduction are tested on a JSM-7100F microscope;

*X-ray photoelectron spectroscopy (XPS)*

XPS is used to analyzed the near-surface valence state of the prepared materials;

*X-ray diffraction (XRD) equipment*

The crystal structure and material types are obtained on a PW101290 1030 (Philips) equipment;

## 5. PROCEDURE TEMPLATE

| Experimental Procedure No. | Experimental Procedure Description | Scale (Mass/Volume) | Location (Fumehood,benctop,etc) | Method New or Existing |
|---|---|---|---|---|
| 4.1 | **Synthesis of size-controlled $Cu_2O$ nanocatalysts** | 0.019 g $Cu(NO_3)_2$; 1.011 g $KNO_3$; 1 M HCl 10mL | Fume hood -7102<br>Ultrasonic – 7102<br>Electrochemical workstation - 7102 | Existing |
| 4.2 | **Electrocatalytic Performance Test** | 2.002 g $KHCO_3$ | Fume hood -7102<br>Ultrasonic – 7102<br>Electrochemical workstation - 7102 | Existing |
| 4.3 | **Sample Characterization** | N/A | | Existing |

# 6. HAZOP Template

## Hazard and Operability Analysis

**4.1 Synthesis of size-controlled $Cu_2O$ nanocatalysts**

| NO | HAZARD | HAZARD EFFECT | SEVERITY | PROBABILITY | RISK | MINIMISE RISK BY | RESIDUAL RISK |
|---|---|---|---|---|---|---|---|
| 1 | Contact with chemicals | Causes severe skin and eye burns. | H | M | H | Wear protective gloves, face shield and lab coats; Conduct experiments in the fume hood | L |
| 2 | Powder inhalation | Harmful by inhalation. | M | M | M | Take the measurement within the fume hood | L |
| 3 | Hot surface of the oven | Skin burn if touched. | M | M | M | Set a warning sign and operate with protective gloves. The hot metal is equipped with a thermal couple. | L |
| FINAL ASSESSMENT: | | | | | | OVERALL RISK: | L |

Remark: Severity–Low:1 (Minor injuries, first aid); Medium:2 (Hospitalization, medical leave); High:3 (Serious injuries, fatality)
Probability–Unlikely:1; Possible:2; Very Likely: 3.

# HAZOP Template
# Hazard and Operability Analysis

## 4.2 Electrocatalytic Performance Test

| NO | HAZARD | HAZARD EFFECT | SEVERITY | PROBABILITY | RISK | MINIMISE RISK BY | RESIDUAL RISK |
|---|---|---|---|---|---|---|---|
| 1 | Contact with chemicals | Causes severe skin and eye burns. | H | M | H | Wear protective gloves, face shield and lab coats; Conduct experiments in the fume hood | L |
| 2 | Powder inhalation | Harmful by inhalation. | M | M | M | Take the measurement within the fume hood | L |
| 3 | Hot surface of the oven | Skin burn if touched | M | M | M | Set a warning sign and operate with protective gloves. The hot metal is equipped with a thermal couple. | L |
| FINAL ASSESSMENT: RISK: | | | | | | OVERALL | L |

# HAZOP Template
# Hazard and Operability Analysis

## 4.3 Sample Characterization

| NO | HAZARD | HAZARD EFFECT | SEVERITY | PROBABILITY | RISK | MINIMISE RISK BY | RESIDUAL RISK |
|---|---|---|---|---|---|---|---|
| 1 | Wrong operation | Personal injury; Property loss | H | M | H | Being well trained and operating according to the instruction of the manual | L |
| FINAL ASSESSMENT: RISK: | | | | | | OVERALL | L |

## 7. Operating Conditions

**Synthesis of size-controlled $Cu_2O$ nanocatalysts**

**Electrocatalytic Performance Test**

- Pressure : atmospheric during preparation
- Temperature : ~25 °C, room temperature
- Flow rates : batch operations therefore not applicable

## 8. Services List

Electricity (AC 220V, 50Hz)

Double de-ionized water

Tap water

Standard fume hood

## 9. Chemicals List

| Chemical | Purity | Quantity per Experiment |
|---|---|---|
| $Cu(NO_3)_2$ (1) | 99 % | 0.019 g |
| $KNO_3$ (2) | 99 % | 1.011 g |
| $HCl$ (3) | 36.5 % | 0.5 mL |
| $KHCO_3$ (4) | 99.99 % | 2.002 g |
| $CO_2$ (5) | 99.5 % | ~200 mL |
| | | |

## 10. Biological Agents List

N/A

## 11. Summary of Relevant Hazards and Incompatibilities

| Material | Summary of Hazards | Incompatibilities |
|---|---|---|
| $Cu(NO_3)_2$ (1) | May intensify fire, oxidizer, Harmful if swallowed, Causes severe skin burns and eye damage | Combustibles, heat |
| $KNO_3$ (2) | May intensify fire, oxidizer, Harmful if swallowed, | Combustibles, heat |
| $HCl$ (3) | Causes severe skin burns and eye damage, May cause respiratory irritation | Bases, Amines, Alkali metals, Metals, permanganates, e.g. potassium permanganate, Fluorine, metal acetylides, hexalithium disilicide |
| $KHCO_3$ (4) | May cause eye, skin, and respiratory tract irritation | Acids; heat. |
| $CO_2$ (5) | Contains gas under pressure; may explode if | Certain reactive metals, hydrides, |

| | | |
|---|---|---|
| | heated. May displace oxygen and cause rapid suffocation. May cause frostbite. May increase respiration and heart rate | moist cesium monoxide, or lithium acetylene carbide diammino may ignite. Passing carbon dioxide over a mixture of sodium peroxide and aluminum or magnesium may explode. |

## 12. Waste List

(1) Mixture of HCl, copper nitrate, potassium nitrate in water, to metal waste container ( 2 L/week).

## 13. Assessment of Significant Risks

(1) Contact with hazard chemicals during the weighing, dissolving and also handling, probably cause skin burn, eye damage without proper protection.
(2) Hand cut may happen if not proper use of the knife for the slicing of the copper foam electrode.
(3) $CO_2$ gas cylinder may cause explosion if not handling properly or with strong impact.
(4) $CO_2$ gas may cause suffocation if large amount of leakage happened with poor ventilation.

## 14. Safety Precautions

*Safety Training Required*

The researcher must attend regular courses (and in some courses obtain a passing result) offered by the Safety and Environmental Office of the University (HKUST) and understand thoroughly the safety concepts of these courses and be able to apply them before being allowed to conduct any experiments or use any of the equipment associated.

The researcher must understand and be aware of all the procedures for handling, and in some cases dealing, with all possible emergency situations and scenarios.

The researcher must undergo training in handling equipment and conducting experiments competently before performing it on his/her own.

Equipment training offered by technical staff for nitrogen adsorption (Omnisorp 100CX), ICP (Perkin Elmer Optima), Elemental Analyser (Vario ELII Eliminator), TGA (Shimadzu TGA-50) are required before conducting the tests.

XRD, SEM, XPS, TEM etc. will be conducted by the technical staff of the MCPF.

*General Laboratory Safety Rules*

It is HKUST policy to ensure that employees and students who are engaged in potentially hazardous operations receive both general and job-specific safety training prior to conducting these operations. Each department will establish a management scheme to implement this policy. Each supervisor will evaluate the nature of the work and will determine what safety training is needed for employees and students under his/her supervision.

General safety courses listed below cover a wide variety of safety issues. In addition to assigning employees and students to attend these courses, supervisors shall also provide job-specific safety training to ensure the safe performance of potentially hazardous operations.

Mandatory Courses (Chemical Safety II / Hazardous Waste Management, MC03; Pressure Safety, MC05; Chemical Safety I / Chemical Safety for Laboratory Users, MC07) and Discretional Courses (Fire Safety and Fire-fighting Equipment, DC03) should be taken in terms of this project.

*Personal Protective Equipment*

Laboratory coat, safety goggles, and nitrile/polyvinyl alcohol gloves because of the presence of solvents such as toluene (from Instant Glove + CPC Database) as the outer layer with rubber gloves as the

inner layer must be worn at all times when performing the experiments, transporting, handling and cleaning chemicals and equipment and clearing chemical spills.

Dust mask should be worn when collecting and weighing solid particles.

Heat resistant gloves will be worn when handling hot items.

*Handling Organic Compounds*

Personal Protective Equipment should be used when handling organic compounds. When disposing of organic waste, organic solvents with halogens (e.g. trichloromethane, trichloroethylene, and dichloromethane) should be collected in "Halogenated Solvents" container and other liquid organic compounds with halogens. "Non-halogenated Solvents" container is for organic solvents and other organic compounds without halogens (e.g. acetone, hexane, and petroleum ethers).

*Handling Flammable Liquid*

Carefully read the manufacturer's label on the container of any flammable liquid before storing or using it. Practice good housekeeping in flammable liquid storage areas. Clean up spills immediately then place the cleanup rags in a closed, bottom ventilated, metal container. Only use approved metal safety containers or the original manufacturer's container to store flammable liquids. Keep the containers closed when not in use; stored away from exits or passageways.

*Handling Heat Process*

Be aware of heat process and mind high temperature equipment, especially the temperature controller. Don't touch the high temperature unit directly.

## 15. Action in Case of Abnormal or Emergency Situations

**(A) In case of loss of containment or accidental spillage**

(1) Minor spillage (<100mL)
Alert co-workers
If safe to do so, confine the spill with appropriate material and/or turn off remotely all heat/ignition sources if flammable vapour is involved.
Ask for assistance is necessary.
Press the emergency ventilation button (do not activate this button in case of fire).
Inform the security office at x8999 or 23588999 with mobile phone when it is safe to do so.
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.

(2) Solid chemicals
Alert co-workers
If safe to do so, confine the spill with appropriate material and/or turn off remotely all heat/ignition sources if flammable vapour is involved.
Ask for assistance is necessary.
If confident, clean the spillage properly, being protected by Personal Protective Equipment.

(3) Major spillage (>1L)
Alert co-workers
If safe to do so, confine the spill with appropriate material and/or turn off remotely all heat/ignition sources if flammable vapour is involved.
Ask for assistance is necessary.
Press the emergency ventilation button (do not activate this button in case of fire).

Inform the security office at x8999 or 23588999 with mobile phone when it is safe to do so.
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.

**(B) Fire-fighting measures**

**When the fire alarm is heard**

- Check if there is any sign of fire in the vicinity.
- If there is fire or smoke, or there is an announcement to evacuate, then evacuate to the assembly point as far as practicable and report to the fire & safety officer.
- If there is no sign of a fire, stay alert and pay attention to announcement until the fire alarm is silenced.
- Evacuate if the alarm has sounded for more than two minutes.
- If the buzzer sound which indicates fire alarm is activated in an adjacent fire zone is heard, stay alert and pay attention to announcement.
- If both the buzzer and the fire alarm are heard, treat as if the fire alarm is heard.

**If a fire is discovered**

- Perform emergency shut down procedures if possible.
- Activate the fire alarm by pressing the break glass fire alarm button.
- Report to Security Control Centre by dialing 8999.
- Alert other people. If safe to do so, try to put out the fire by firefighting equipment.
- Do not take any personal risk. If the fire gets beyond control, evacuate immediately as listed above.
- Close the door of the room on fire.

**Firefighting equipment**

- Water from the hose reels is good for wood and paper fire, structural fire, but not for oil, electrical or metal fire.
- The most common fire extinguishers on campus is the carbon dioxide type (black container) which are good for general purposes, including oil and electrical fire.
- Some laboratories have dry powder fire extinguishers (blue container), which are good for chemical fire, including metal fire.
- Sand can be used to contain flammable liquid as well as put out a fire, including metal fire.
- Fire blanket can be used when someone's clothing catches fire.

**Evacuation procedures**

- Remain calm. Walk; do not run, especially when travelling on staircases.
- Immediately leave the building and go to the assembly point using the nearest exit.
- Try to help those who may have difficulties traveling such as disabled and pregnant persons.
- Do not use the lifts.
- Report to your Fire & Safety Officer at the assembly point as far as practicable.
- Do not return to the building until permission is given by the Fire Services Department Officer in charge of the scene.

**When clothing is on fire**

- Do not run
- Drop to the floor and roll to extinguish the fire.
- If fire blanket is available, wrap around body to help smother the fire.