SYNTHESIS AND CHARACTERIZATION OF UNSUPPORTED COPPER SULFIDE FOR MERCURY TRAPPING IN AQUEOUS SYSTEM

YAP PEI LAY

DISSERTATION SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR

2012

UNIVERSITI MALAYA

ORIGINAL LITERARY WORK DECLARATION

Name of Candidate: **YAP PEI LAY** (I.C No: **850429145802**)

Registration/Matric No: **SGR 100020**

Name of Degree: **MASTER OF SCIENCE**

Title of Project Paper/Research Report/Dissertation/Thesis ("this Work"):

SYNTHESIS AND CHARACTERIZATION OF UNSUPPORTED COPPER SULFIDE FOR MERCURY TRAPPING IN AQUEOUS SYSTEM

Field of Study: **MATERIAL SCIENCE**

I do solemnly and sincerely declare that:

(1) I am the sole author/writer of this Work;
(2) This Work is original;
(3) Any use of any work in which copyright exists was done by way of fair dealing and for permitted purposes and any excerpt or extract from, or reference to or reproduction of any copyright work has been disclosed expressly and sufficiently and the title of the Work and its authorship have been acknowledged in this Work;
(4) I do not have any actual knowledge nor do I ought reasonably to know that the making of this work constitutes an infringement of any copyright work;
(5) I hereby assign all and every rights in the copyright to this Work to the University of Malaya ("UM"), who henceforth shall be owner of the copyright in this Work and that any reproduction or use in any form or by any means whatsoever is prohibited without the written consent of UM having been first had and obtained;
(6) I am fully aware that if in the course of making this Work I have infringed any copyright whether intentionally or otherwise, I may be subject to legal action or any other action as may be determined by UM.

Candidate's Signature Date

Subscribed and solemnly declared before,

Witness's Signature Date

Name: **DR. SHARIFAH BEE ABD HAMID**
Designation: **PROFFESSOR**

ABSTRACT

Two phase pure copper sulfides, rhombohedral phase *digenite* (Cu_9S_5) and hexagonal phase *covellite* (CuS) have been successfully prepared via hydrothermal method using copper nitrate and sodium thiosulfate without any assisting agent. The structural, chemical, and thermal properties of the as-synthesized phase pure systems were investigated with various characterization techniques, including powder X-ray diffraction (PXRD), scanning and transmission electron microscopy (SEM and TEM), BET gas sorption, X-ray fluorescence (XRF), energy dispersive X-ray scpectroscopy (EDX), thermogravimetric analysis coupled to mass scpectroscopy (TGA-MS), as well as differential scanning calorimetry (DSC) methods. In this study, the phase pure *covellite* has shown a potential ability to remove Hg(II) in aqueous system with maximum sorption capacity of *ca.* 400 mg/ g can be reached at pH 4. The collected experimental data is best fitted to Langmuir isotherm and the sorption of Hg(II) onto *covellite* in aqueous system is favored in a wide range of pH. This was supported by the calculated thermodynamic parameter, $\Delta G°$ which has shown that the sorption of Hg(II) onto *covellite* is favorable in a wide range of pH, particularly at low pH. Apart from that, three synthesis parameters (synthesis temperature, Cu: S mole ratio, and synthesis time) have been systematically investigated throughout the study. It was found that synthesis temperature and Cu: S mole ratio determined the phase purity, crystal phase, and morphology of the final products formed; while synthesis time has pronounced effect on the crystallite size of the yields. Furthermore, several mechanistic pathways leading to the final formation of *covellite* were proposed and discussed based on the detailed analysis of PXRD done at different synthesis temperatures. This current study also revealed that the renowned most stable phase in copper sulfide family, *covellite* has transformed into a

mixed phase of pentahydrate copper sulfate and *covellite* at ambient condition after a certain period. It could be shown that *covellite* is an air-sensitive material which undergoes structural changes after exposure to moisture or air. This discovery was supported with various observations from PXRD, EDX, and TG-MS techniques. Therefore, phase stability study was conducted to find out the most efficient way to store copper sulfides besides to investigate the stability of *covellite* over a series of time at ambient condition. The phase stability experiments indicated that *covellite* with the common washing and storage methods described in the research methodology was stable up to 4 weeks. *Covellite* with the purging of nitrogen gas before storage is the best method to prevent *covellite* from further oxidation.

ABSTRAK

Dua fasa tulen kuprum sulfida, iaitu rombohedral *digenite* (Cu_9S_5) dan heksagonal *covellite* (CuS) telah berjaya disediakan melalui kaedah hidroterma dengan menggunakan kuprum nitrat dan natrium thiosulfat tanpa ejen pembantu. Sifat-sifat struktur, kimia, dan terma bagi dua sistem fasa tulen telah dicirikan dengan menggunakan pelbagai kaedah pencirian termasuk kaedah serbuk pembelauan sinar-X (PXRD), mikroskop elektron imbasan dan transmisi (SEM & TEM), penjerapan dan penyahjerapan gas nitrogen (BET), (XRF), taburan tenaga sinar-x (EDX), termagravimetrik-jisim spektroskopi (TGA-MS), dan perbezaan imbasan tenaga (DSC). Dalam kajian ini, fasa tulen *covellite* telah menunjukkan keupayaan untuk menyingkirkan Hg(II) dalam sistem akueus dengan kapasiti penjerapan maksimum yang dicapai ialah kira-kira 400 mg/ g pada pH 4. Data eksperimen yang dikumpul adalah sangat bersesuaian dipadankan dengan isoterma Langmuir dan penjerapan Hg(II) oleh *covellite* adalah cenderung dalam lingkungan pH yang luas di dalam sistem akueus. Perkara ini adalah disokong dengan parameter termodinamik, $\Delta G°$ yang menunjukkan penjerapan Hg(II) oleh *covellite* adalah cenderung dalam lingkungan pH yang luas, terutamanya pada pH yang rendah. Selain itu, tiga parameter sintesis (suhu sintesis, nisbah mol Cu: S, dan masa sintesis) telah diselidik dengan bersistematik dalam kajian ini. Suhu sintesis dan nisbah mol Cu: S didapati boleh menentukan fasa tulen, fasa kristal, dan morfologi bagi produk terakhir yang dihasilkan; manakala masa sintesis mempunyai kesan yang ketara dalam saiz kristalit hasil produk.Tambahan pula, beberapa mekanisme yang menunjukkan pembentukan *covellite* telah dicadangkan dan dibincangkan berdasarkan analisis PXRD yang dijalankan secara terperinci pada suhu sintensis yang berbeza. Kajian ini juga menunjukkan bahawa *covellite*, iaitu fasa yang terkenal dengan

kestabilannya dalam keluarga kuprum sulfida, telah tertransformasi kepada fasa campuran kuprum sulfat pentahidrat dan *covellite* pada keadaan ambien selepas suatu jangka masa. Fenomena ini menujukkan bahawa *covellite* ialah bahan yang sensitif kepada udara dan boleh menjalani perubahan struktur apabila terdedahkan kepada air atau udara. Penemuan ini disokong dengan beberapa perubahan sifat-sifat yang didapati daripada teknik-teknik pencirian seperti PXRD, EDX, dan TG-MS. Oleh sebab itu, kajian fasa kestabilan telah dijalankan untuk mengetahui cara yang sesuai untuk menyimpan kuprum sulfida selain untuk menyelidik kestabilan *covellite* dalam satu siri masa yang tertentu pada keadaan ambien. Ekeperimen fasa kestabilan menunjukkan bahawa *covellite* yang disediakan dengan cara pembasuhan dan penyimpanan yang dihuraikan dalam metodologi penyelidikan ini stabil sehingga 4 minggu. *Covellite* yang disediakan dengan kaedah penyemburan gas nitrogen adalah cara yang terbaik untuk mengelakkan *covellite* daripada proses pengoksidaan yang seterusnya.

ACKNOWLEDGEMENTS

First and foremost, it is my pleasure to thank everyone who has assisted me throughout the journey of completing my master degree. Hereby, I wish to extend my heartfelt gratitude to Prof. Dr. Sharifah Bee Abd Hamid, my supervisor for her advice, assistance, and guidance besides providing me this golden opportunity to involve in this interesting research project. I faithfully wish that the investigation and exploration done on this research topic would lead to a greener, safer, and cleaner dwelling sites which could promote a mercury-free environment to the ecosystems.

My sincere appreciation also goes to Prof. Robert Schlögl, director of Inorganic Chemistry Department, Fritz Haber Institute of the Max Planck Society for his willingness to accommodate my research attachment (about 6 months) in Fritz Haber Institute besides introducing this meaningful project to me. The research experience which I have gained is indeed cultivating my research interest in this respective discipline. I personally very much inspired by his dedication, and determination in pursuing his dreams in research.

I would like to convey my sincere credit to my co-supervisors, Dr. Malte Behrens and Dr. Olaf Timpe for their valuable scientific contributions and useful comments in realizing the truth and facts in science. Not forgotten, great appreciation also goes to Dr. Muralithran Kutty and Dr. Looi Ming Hong for their enthusiasm in sharing their ideas and thoughts.

Besides that, I would like to acknowledge my research partner, Au Yoong Yow Loo for his everlasting support, and useful scientific insights from time to time. I would also like to express my sincere thanks to COMBICAT science officers, all the members of Inorganic Chemistry Department in Fritz Haber Institute, especially those of Nanostructures group for aiding me with sample characterizations as well as technical support besides creating a motivated and enjoyable working environment. I have truly benefited from my research attachment in Berlin.

Furthermore, this research voyage would not have been smoothly sailed without the endurance, encouragement, and moral support from my beloved family and my dear friends. I am grateful for their unconditional love and understanding which have brought me this far.

Last but not least, my special thanks to the financial support from University of Malaya Fellowship Scheme (SBUM) for covering my master studies, Research University Grant, (UMRG: RG022-09AET), and Postgraduate Research Grant (PPP: PS376-2010B) for research funds.

Yap Pei Lay (Emily), 2012.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS AND ABBREVIATIONS

BET	Brunauer-Emmett-Teller
C_2H_5NS	thioacetamide
C_2H_5OH	ethanol
$C_3H_7NO_2S$	L-cysteine
CS_2	carbon bisulfide
CTAB	cetyl trimethyl ammonium bromide
$Cu(ac)_2$	copper (II) acetate
Cu_2S	chalcocite
$Cu_{31}S_{16}$	djurleite
$Cu_{39}S_{28}$	spionkopite
Cu_5FeS_4	bornite
Cu_7S_4	anilite
Cu_8S_5	geerite
Cu_9S_5	digenite
Cu_9S_8	yarrowite
$CuFe_2S_3$	cubanite
$CuFeS_2$	chalcopyrite
CuO	copper oxide
CuS	covellite
CuS_2	villamaninite
$CuSO_4$	copper (II) sulfate
DMDTC	dimethyldithiocarbamate
DSC	Differential Scanning Calorimetry
DTO	dithiooxamide

EDX	Energy Dispersive X-ray Spectroscopy
FeS_2	pyrite
FESEM	Field Emission Scanning Electron Micrscopy
GEb	percentage calculated with reference to global emmision
HgS	cinnabar
HRTEM	High Resolution Transmission Electron Microscopy
HSAB	Hard Soft Acid Base
ICP	Inductive Coupled Plasma
K	kelvin
K_{sp}	solubility product constant
LNG	liquefied natural gas
Mg	megagram
MS	Mass Spectroscopy
ng	nanogram
PCP	phenylcyclidine
ppb	parts per billion
Ppk	polyphosphate kinase
ppm	parts per million
PVC	polyvinyl chloride
SAMMS	Self Assembled Monolayers on Mesoporous Silica
SDBS	4-dodecylbenzenesulfonic acid
SDS	sodium dodecyl sulfate
TC	thiocarbonate
Tg	teragram
TGA	Thermogravimetric Analysis

TiO_2	titanium dioxide
TMR	Total Mercury Removal
TMT	2, 4, 6-trimercaptotriazine
TNT	trinitrotoluene
UNEP	United Nations Environmental Programme
US EPA	United States Environmental Protection Agency
UV	ultraviolet
VCM	vinyl chloride monomer
PXRD	Powder X-ray Diffraction
XRF	X-ray Fluorescence
yr	year

LIST OF APPENDICES