SYNTHESIS AND THERMAL CONDUCTIVITY OF COPPER NANOPARTICLE ENCAPSULATED BY GRAPHENE

by

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

µm	Micron
3D	Three-dimensional
Ar	Argon
at.	Atomic
C	Carbon
CH_4	Methane
CNF	carbon nanofiber
CNT	Carbon nanotube
Co	Cobalt
Co-MgO	Cobalt supported on MgO
CSP	Concentrated Solar Power
Cu	Copper
$CuCl_2$	Copper chloride
Cu-MgO	Copper supported on MgO
CuO	Copper oxide
CuO-MgO	Copper oxide supported on MgO
CVD	Chemical vapor deposition
dTG	Differential thermogravimetric
DWNT	Double-walled nanotube
EDS	Energy dispersive X-ray spectrometry
eV	ElectronVolt
Fe	Iron
Fe-MgO	Iron supported on MgO

FFT	Fast Fourier transform
g	Gram
GNP	Graphene nanoplatelet
h	Hour
H	Hydrogen
H_2	Hydrogen gas
He	Helium
HRTEM	High-resolution transmission electron microscope
HTF	Heat transfer fluid
kV	KiloVolt
Mg	Magnesium
mg	Milligram
$Mg(OH)_2$	Magnesium hydroxide
MgO	Magnesium oxide
min	Minute
mL	Milliliter
mm	Millimeter
mol.	Mole
MPa	MegaPascal
MWNT	Multi-walled nanotube
N	Nitrogen
N/A	Not applicable
N_2	Nitrogen gas
Ni	Nickel
nm	Nanometer

O	Oxygen
PCM	Phase change material
PMMA	Poly(methyl methacrylate)
ppm	parts per million
PV	Photovoltaic
R&D	Research and development
RBM	Radial breathing mode
RT	Room temperature
SAED	Selected area electron diffraction
sccm	Standard cubic centimeter
SEM	Scanning electron microscope
SWNT	Single-walled nanotube
TEM	Transmission electron microscope
TES	Thermal energy storage
TGA	Thermogravimetric analysis
TPS	Transient plane source
USD	United States Dollar
v/v	Volume/volume
vol.	Volumetric
wt.	Weight
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence

LIST OF SYMBOLS

%	Percent
″	Inch
°	Degree
°C	Degree Celsius
Å	Angstrom
d	D-spacing
m/z	Mass-to-charge ratio
z	Charge
θ	Theta
λ	Wavelength

SINTESIS DAN KEBERALIRAN HABA NANOZARAH KUPRUM YANG DIBALUT OLEH GRAFENA

ABSTRAK

Kaedah mudah aplikasi pemendapan wap kimia (CVD) telah digunakan untuk mensintesis grafena yang dimangkin oleh kuprum yang disokong di atas MgO. Penggunaan komposit grafena-CuO-MgO (iaitu produk selepas proses CVD) sebagai bahan tambah untuk meningkatkan keberaliran haba dalam bahan penyimpan tenaga haba juga dikaji. CuO-MgO telah disediakan dengan memendap kuprum berzarah nano di atas permukaan serbuk MgO dengan menggunakan teknik impregnasi. Kajian melalui mikroskop pengimbas elektron digandingkan dengan teknik serakan tenaga sinar-X menunjukkan yang zarah-zarah kuprum berskala nano telah dimendapkan secara seragam di atas permukaan MgO. Pertumbuhan grafena dilakukan pada tekanan atmosfera di dalam sebuah reaktor unggun tetap yang mendatar tanpa adanya langkah penurunan yang khusus sebelum proses tindakbalas CVD; oleh yang demikian, zarah kuprum berada dalam keadaan oksida semasa proses pertumbuhan grafena berlaku. Mekanisme pertumbuhan grafena di atas kuprum oksida telah dikaji dengan teliti dengan menggunakan spektroskopi fotoelektron sinar-X dan pembelauan sinar-X. Buat pertama kalinya dibuktikan dengan jelas bahawa kuprum (5 mol.%) dalam bentuk oksida, secara efektif memangkin pertumbuhan grafena yang berlapis nipis apabila tindakbalas CVD dijalankan pada suhu 950 °C selama 60 min, 980 °C selama 30 min and 1000 °C selama 30 min di bawah aliran gas metana (50 mL/min), nitrogen (100 mL/min) dan hidrogen (100 mL/min). Mekansime pertumbuhan grafena diusulkan mengikut turutan berikut: (i) CuO mengalami proses penurunan oleh gas hidrogen yang

mengakibatkan terbentuknya kekosongan kedudukan atom oksigen pada permukaan, (ii) penyah-hidrogenan terhadap metana pada kedudukan tersebut, dan (iii) seterusnya pembentukan jaringan grafitik yang menjadikan lapisan-lapisan grafena. Berdasarkan cara alternatif, terus dan tepat menerusi analisis termogravimetri, kandungan grafena yang tinggi berjaya dihasilkan (lingkungan 9.6 % dalam peratusan jisim) apabila tindakbalas CVD dijalankan pada suhu 1000 °C selama 30 minit. Berbanding dengan kaedah lain yang sedia ada, kaedah mensintesis grafena yang digunakan di dalam kajian ini adalah lebih cekap (125 % dalam peratusan jisim terhadap pemangkin) dan memberikan kadar pertumbuhan grafena yang tinggi (42 mg/ min/ g pemangkin) serta dihasilkan pada kos yang lebih rendah disebabkan oleh penggunaan bahan mentah yang lebih murah. Bahan yang dihasilkan selepas CVD (iaitu grafena beserta CuO-MgO) berpotensi tinggi untuk digunakan dalam aplikasi penyimpanan tenaga haba kerana ia dijangka boleh meningkatkan mutu kebolehaliran haba dengan wujudnya rangkaian terus sesama juzuk-juzuk unsur (iaitu antara grafena, CuO dan MgO) bagi saluran pengaliran haba. Berdasarkan data kajian yang diperolehi daripada kaedah sumber alihan tarahan, bahan in memberikan 51% peningkatan terhadap keberaliran haba terhadap bahan penyimpan haba.

SYNTHESIS AND THERMAL CONDUCTIVITY OF COPPER NANOPARTICLE ENCAPSULATED BY GRAPHENE

ABSTRACT

A facile chemical vapor deposition (CVD) method was used to synthesize graphene, which was catalyzed by copper supported on MgO. The use of graphene-CuO-MgO composite (i.e. the product after CVD) as additive for thermal conductivity enhancement in thermal energy storage material was also investigated. CuO-MgO was prepared by depositing 5 mol. % of copper nanoparticle on MgO powder using an impregnation technique. Investigation under scanning electron microscope coupled with energy dispersive X-ray spectrometry revealed that the copper nanoparticles were evenly deposited on the surface of MgO powders. The CVD process was carried out at atmospheric pressure in a horizontal fixed bed reactor without a dedicated reduction step prior to CVD reaction process; hence copper nanoparticle was in its oxidized state during the growth process of graphene. The mechanism by which graphene grows on copper oxide was deeply investigated by X-ray photoelectron spectroscopy and X-ray diffraction. For the first time, it was unambiguously proven that copper oxide (5 mol.%) efficiently catalyze the growth of few- and multi-layered graphene when the CVD reaction was conducted at 950 °C for 60 min, 980 °C for 30 min and 1000 °C for 30 min under the flow of methane (50 mL/min), nitrogen (100 mL/min) and hydrogen (100 mL/min). The mechanism of graphene growth was proposed in the following order: (i) reduction process of CuO by hydrogen that creates oxygen vacancies on the surface, (ii) methane dehydrogenation on the oxygen vacancy site and (iii) subsequent construction of graphitic network forming graphene layers. Based on the result from an alternative,

direct and accurate approach of thermogravimetric analyses, high content of graphene was able to be produced (around 9.6 wt. %) when the CVD reaction was conducted at 1000°C for 30 min. Compared to the existing methods, this corresponds to a high efficiency (125 wt.%) and growth rate of graphene (42 mg/ min/ g of catalyst), produced at a considerably lower cost since cheaper raw materials were utilized. The as-produced material after CVD (i.e. graphene together with CuO-MgO) has high potential to be used in thermal energy storage applications due to the expected high thermal conductivity enhancement it could offer from the establishment of direct contact between the constituents, i.e. graphene, CuO and MgO, forming an interconnected network for heat conduction pathway. Based on the thermal investigation using a transient plane source method, 51% enhancement to the thermal conductivity of the thermal storage material was recorded.

CHAPTER ONE

INTRODUCTION

This chapter presents the background of the current research work which covers topics such as graphene, renewable energy and thermal energy storage for solar applications. Separate sections are assigned for each of these topics. Then, the motivations of the present work are expressed after identifying the current issues faced. A set of objectives are outlined and the scope of the present study is described. Finally, the organization of chapters in this thesis is given.

1.1 Graphene

Graphene, a one-atom thick film of sp^2-bonded carbon atom with hexagonal arrangement, has ignited strong interest from the scientific community ever since its discovery in 2004 by Professor Andre Geim and Professor Konstantin Novoselov from the University of Manchester, United Kingdom. This discovery won them the Nobel Prize in Physics 2010 for "groundbreaking experiments regarding the two-dimensional material graphene". The high attention toward graphene is due to its unique properties that have not been previously observed in other nanomaterials such as outstanding electronic properties (Novoselov et al., 2005; Bonaccorso et al., 2010), superior optical (Bonaccorso et al., 2010; Li et al., 2009a) and mechanical (Lee et al., 2008) properties as well as exceptional ability to conduct electricity (Li et al., 2009a) and heat (Ghosh et al., 2008; Balandin et al., 2008). The combination of these incredible properties allows it to be used, in the future, in myriad applications such as sensors and biosensors (Liu et al., 2015; Green and Norton, 2015), bioengineering (Gao and Duan, 2015), biomedical (Liu et al., 2013; Krishna et al.,

2013), composite materials (Wang et al., 2014a), energy technology (Hu et al., 2015; Wang and Liu, 2015) and solar cells (Das et al., 2014).

The discovery of graphene had brought forth new area of carbon nanomaterials after carbon nanotubes (CNTs). Since its discovery, research and technology innovations based on graphene has been rising exponentially. The number of patent applications and granted patents on graphene has even surpassed that of CNTs in 2013 and 2014 (Zurutuza and Marinelli, 2014). Based on the latest data on the worldwide patent landscape from the Informatics team at the UK Intellectual Property Office (2015), there are over 25,000 published patents related to graphene from 2005 to 2014 as compared to only 50 patents application submitted prior to that. It is natural to expect growth in graphene innovations in 2015 and beyond considering the observed upward trend.

Despite many significant breakthroughs in the laboratories, the commercial adoption of graphene is deemed slow (Zurutuza and Marinelli, 2014; Levchenko et al., 2016) and many of its touted application is yet to be fully materialized. One of the main reasons for this is related to the problem of high production cost for graphene, thus limiting their scalability from the laboratory tested techniques (Raccichini et al., 2014; Novoselov et al., 2012). In this scenario, closing the gap between laboratory-scale research and practicle applications has beeen one of the main agenda among research scientists. This effort is important in order to meet its increasing demand for the coming years. Graphene markets is projected to grow from USD 20 million in 2014 to more than USD 390 million in 2024 (ReportBuyer, 2015). One major sector that graphene is expected to be heavily invested upon is in the area of renewable energy (Novoselov et al., 2012).

1.2 Solar thermal energy storage

A shift towards green energy and power generation from renewable resources has garnered increasing interest worldwide (IRENA, 2015) due to great concern over the depletion of fossil fuels and also the climate change and greenhouse emissions brought by the usage of these conventional energy sources. In this situation, harnessing power from natural resources such as solar, wind, hydro, ocean, geothermal and biomass for renewable energy is undoubtedly the best option because it can offer sustainable energy generation and certainly can minimize the negative impact to the environment. Rapid deployment of technologies based on renewable energies such as solar photovoltaic (PV) technologies (Radomes Jr and Arango, 2015; Ghafoor and Munir, 2015), solar thermal concentrating solar power (CSP) (Nonnenmacher et al., 2016), on- and off- shore wind energy (Zhao et al., 2015), hydropower (Hennig, 2016) and bio-energy (Guo et al., 2015) has been established around the world and they are projected to grow substantially in the coming years (IRENA, 2015) to meet the increasing energy demand.

Globally, there is a good mix of the technologies based on renewable energy that are currently being heavily utilized for energy generation such as solar photovoltaic in Germany, solar CSP in Spain, on-shore wind power in the United States, hydropower in China, biomass in Finland and geothermal energy in Indonesia. The type of technology being deployed is inherently governed by specific geographical factors whereas different parts of the world vary by the different types of natural abundance and energy requirements. However, the current global energy provider is still dominated by fossil fuels, while renewable energy accounts to around 13.5% of the global energy demand (Sahoo, 2016). The main drawback of renewable energy sources is that they are naturally intermittent and this may generate high

fluctuations of power output that would hinder power network stability and reliability (Luo et al., 2015). The use of energy storage is very important to deal with this issue in order to make these renewable sources more stable and dependable for practical applications (Daim et al., 2012). This is done by storing the excess energy being generated and then released for later use when needed (Hadjipaschalis et al., 2009). Therefore, technologies based on energy storage will play a crucial role in achieving a solid, efficient and cost-effective power distribution from renewable energy towards becoming the main energy contributors for the society's energy supply (Kousksou et al., 2014).

Solar energy has been touted as the type of renewable energy with the brightest future due to its supreme resource potential compared to other renewable alternatives (Lewis, 2016; Khan and Arsalan, 2016). In the past decade, research and development (R&D) efforts and deployment activities concerning the utilization of solar energy has been intensified. Solar-derived PV and CSP are the two most prominent technologies in this sector (Lewis, 2016). PV dominates CSP in terms of the number of commercial deployment of power plant and worldwide installed capacities due to lower initial investment costs involved (Khan and Arsalan, 2016), but CSP is increasingly competing with PV and the number of countries with installed CSP seems to be rapidly growing (Baharoon et al., 2015). A recent report reveals that CSP plant produces greater energy than PV plant for the same nominal power output which suggests that the economic returns of CSP plant is, somehow, greater than a PV plant (Khan and Arsalan, 2016).

Figure 1.1 shows the schematic diagram of a CSP power plant that uses a two-tank direct system. The CSP generates electricity through sunlight which is concentrated by arrays of mirrors (heliostats) to heat a molten salt used as heat

transfer fluid (HTF) in a receiver tube. The heated HTF is stored in the hot tank that could be used during non-sunlight periods by producing a steam which drives a turbine-generator set through heat exchangers. The cooled HTF is pumped and stored into the other tank for a heating cycle, thereafter.

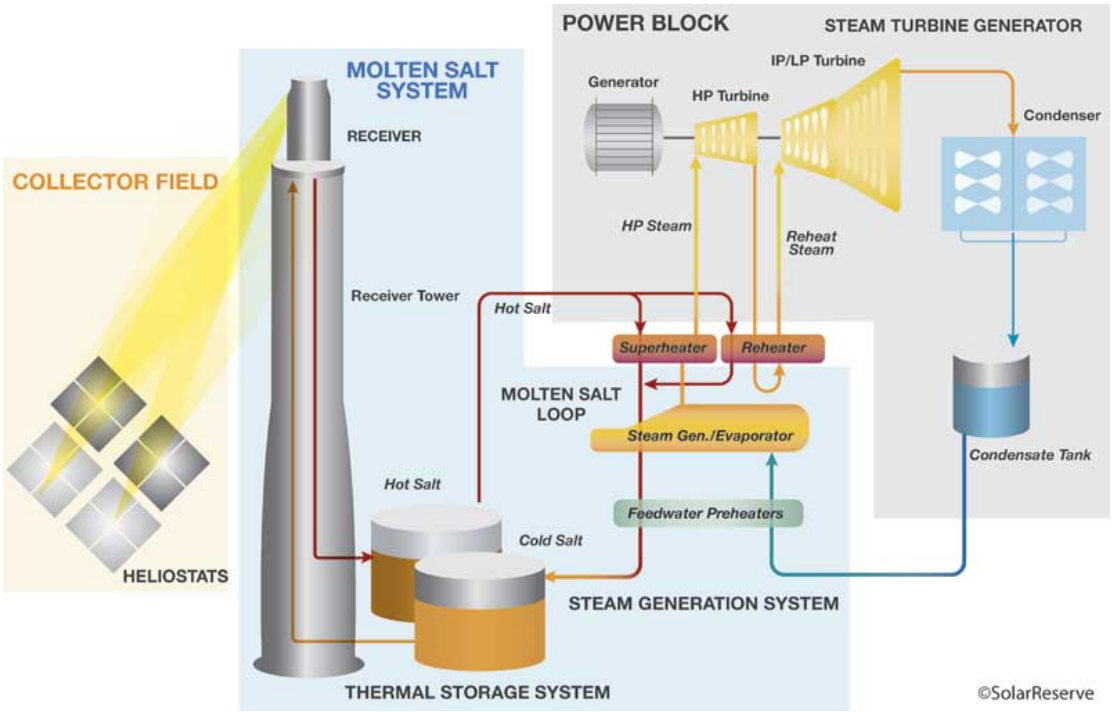

Figure 1.1 Schematic diagram of a CSP power plant (SolarReserve, 2016)

In order to make CSP become more cost-effective, improvement in the capabilities of CSP systems for conversion of sunlight into heat is required. In particular, the thermal storage fluids have been pursued as one of the important subject for R&D in order to improve the energy storage capacity by operating at higher temperature (Lewis, 2016; Kousksou et al., 2014; Baharoon et al., 2015; Liu et al., 2012). Currently, many CSP plants especially the parabolic-trough type use synthetic oil as heat transfer fluid. For high temperature (> 400 °C), replacement of oil is required and molten salt- or metal-based phase change material (PCM) were

identified as excellent candidates since they can operate at high temperature due to their high melting temperature.

For solar energy harvesting, latent-heat-based thermal energy storage (TES) system using PCMs has attracted attention because it offers high thermal storage density in comparison to sensible heat storage devices. Previous work has demonstrated that PCM has the capacity to store more heat per volume (around 3 – 4 times) than sensible heat storage material (Mehling and Cabeza, 2008). PCM relies on phase change occurring between liquid and solid states for energy storage and release in an isothermal process. Salt (carbonates, nitrates etc…) and metallic materials are the candidates for PCMs in solar application due to their high melting point. Compared to metallic materials, salts are cheaper but they exhibit lower thermal conductivity which may limit their application. Enhancement of thermal conductivity is required to achieve high heat charging and discharging rates in the salt-based TES system.

Introduction of materials with high thermal conductivity as filler such as carbon-based nanomaterials has been pursued to deal with this issue. Carbon nanofillers such as flaked graphite (Ge et al., 2014a, 2014b), carbon fibers (Elgafy and Lafdi, 2005; Wang et al., 2011; Fan et al., 2013), CNTs (Ye et al., 2014; Wang et al., 2010a; Fan et al., 2013; Wu et al., 2016) and graphene nanosheets/nanoplatelets (Yavari et al., 2011; Fan et al., 2013; Wu et al., 2016; Yuan et al., 2016) have been tested and studied in the past as potential nanofillers for the enhancement of thermal conductivity in PCMs. These carbon allotropes used as additives are good candidates to enhance the thermal conductivity in PCMs due to their excellent intrinsic thermal conductivity and low density.