UNIVERSITI PUTRA MALAYSIA

CHARACTERIZATION AND DISPERSION BEHAVIOR OF TITANIUM DIOXIDE AS PHOTOCATALYTIC NANOPARTICLES USING METAL ORGANIC CHEMICAL VAPOUR DEPOSITION SYSTEM

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By

SITI HAJAR BINTI OTHMAN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor Philosophy

December 2011

To my beloved parents for their great sacrifice..

To my dear husband and son for completing my life..

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor Philosophy

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December 2011

Chair: Suraya Abdul Rashid, PhD

Faculty: Faculty of Engineering

Metal organic chemical vapour deposition (MOCVD) is a favourable technique to synthesize nanoparticles owing to the relative ease and simplicity of the process. In the MOCVD system, the presence of heat decomposes gaseous reactants to form a stable solid product. The motivation of the present work was to study the synthesis, doping, characterization, dispersion, and photocatalytic properties of TiO_2 nanoparticles synthesized via MOCVD. Computational fluid dynamics (CFD) simulation was utilized to provide better understanding on the MOCVD synthesis system as well as fluid dynamics inside the reactor.

It was found that deposition temperature plays an important role in determining the properties of the synthesized TiO_2 nanoparticles such as particle size and crystallinity. Crystallinity was determined to have significant influence on photocatalytic activity compared to particle size. The nanoparticles heat treated at temperatures higher than or equal to the deposition temperature had improved photocatalytic activity. Thus, it was deduced that the choice of heat treatment

temperature should be made in view of the deposition temperature. Fe doping was found to promote the phase transition, slightly decrease the particle size, and enhance the absorption of TiO_2 nanoparticles in the visible spectrum. However, the photocatalytic activity decreased due to the unfavourable location of Fe ion inside the interior matrix of the TiO_2 nanoparticles rather than on the exterior surface.

For the dispersion study, rupture followed by erosion was determined to be the main break up mechanisms when ultrasonication was employed. 3 weight% of polyacrylic acid with average molecular weight of 2000 g/mol was determined to produce the best dispersion and most stable suspension. The coatings were confirmed to be photocatalytically active.

Finally, the CFD simulation results indicate that increasing deposition temperature and reducing carrier gas flowrate increases the surface deposition rate and the amount of TiO_2 nanoparticles produced. Temperature plays remarkable part in determining the rate of surface deposition of TiO_2 nanoparticles compared to carrier gas flowrate. Flow recirculations were found to occur in the reactor due to protrusion and large temperature gradient. Good mixing of N_2 and O_2 gases is important to ensure the deposition uniformity. Good agreement between experimental and simulation results lends support to the reliability of the simulations work.

In conclusion, this work opens the window towards improving and optimizing the synthesis process of nanoparticles via MOCVD method as well as offers knowledge on the dispersion and stabilization of nanoparticles towards advancement for industrial applications.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENCIRIAN DAN SIFAT PENYERAKAN TITANIUM DIOKSIDA SEBAGAI NANOPARTIKEL FOTOKATALITIK MENGGUNAKAN SISTEM PENGENAPAN WAP KIMIA LOGAM ORGANIK

Oleh

SITI HAJAR BINTI OTHMAN

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Pengerusi: Suraya Abdul Rashid, PhD

Fakulti: Fakulti Kejuruteraan

Pengenapan wap kimia logam organik (MOCVD) adalah teknik yang digemari untuk mensintesis nanopartikel relatif dengan kemudahan dan kesederhanaan proses tersebut. Dalam proses MOCVD, kehadiran haba menguraikan gas bahan tindak balas untuk membentuk produk pepejal yang stabil. Motivasi kerja ini adalah untuk mengkaji sintesis, pengedopan, pencirian, penyebaran, dan sifat-sifat fotokatalitik nanopartikel TiO_2 yang disintesis menggunakan MOCVD. Simulasi pengiraan dinamik bendalir (CFD) digunakan untuk memberikan pemahaman yang lebih baik mengenai sistem sintesis MOCVD serta dinamik bendalir di dalam reaktor.

Suhu pengenapan didapati memainkan peranan penting dalam menentukan sifat-sifat nanopartikel TiO_2 yang disintesis seperti saiz partikel dan kristaliniti. Kristaliniti didapati mempunyai pengaruh yang besar ke atas aktiviti fotokatalitik berbanding saiz partikel. Terdapat peningkatan dalam aktiviti fotokatalitik nanopartikel yang dirawat pada suhu yang lebih tinggi daripada atau sama dengan suhu pengenapan. Kesimpulannya, pemilihan suhu rawatan haba perlu dibuat berpandukan suhu

pengenapan. Pengedopan Fe didapati menggalakkan peralihan fasa, mengurangkan sedikit saiz partikel, dan meningkatkan penyerapan nanopartikel TiO_2 ke spektrum boleh lihat. Walau bagaimanapun, aktiviti fotokatalitik berkurangan kerana lokasi ion Fe yang tidak diingini iaitu di dalam matriks dalaman nanopartikel TiO_2 dan bukannya pada permukaan luaran.

Untuk kajian penyerakan, didapati bahawa pemecahan diikuti oleh hakisan adalah mekanisme utama penggunaan ultrasonik. 3% berat asid poliakrilik dengan purata berat molekular 2000 g/mol didapati dapat menghasilkan penyerakan yang terbaik dan ampaian yang paling stabil. Saduran telah disahkan aktif fotokatalitik.

Akhir sekali, keputusan simulasi CFD menunjukkan bahawa kadar permukaan pengenapan dan jumlah nanopartikel TiO_2 yang dihasilkan meningkat dengan peningkatan suhu pengenapan dan pengurangan kadar aliran gas pembawa. Suhu memainkan peranan yang penting dalam menentukan kadar permukaan pengenapan nanopartikel TiO_2 berbanding kadar aliran gas pembawa. Aliran edaran semula didapati berlaku di dalam reaktor kerana jorokan dan perbezaan suhu yang besar. Percampuran yang baik antara gas N_2 dan O_2 adalah penting untuk memastikan keseragaman pengenapan. Persamaan yang baik antara keputusan ujikaji dan simulasi menyokong kredibiliti kerja simulasi.

Kesimpulannya, kerja ini membuka peluang ke arah memperbaiki dan mengoptimumkan proses sintesis nanopartikel menerusi kaedah MOCVD serta menawarkan pengetahuan mengenai penyerakan dan kestabilan nanopartikel ke arah kemajuan untuk aplikasi perindustrian.

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I certify that a Thesis Examination Committee has met on 2 December 2011 to conduct the final examination of Siti Hajar binti Othman on her thesis entitled "Characterization and Dispersion Behavior of Titanium Dioxide as Photocatalytic Nanoparticles Using Metal Organic Chemical Vapour Deposition System" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the student be awarded the Doctor of Philosophy.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of **Doctor of Philosophy**. The members of the Supervisory Committee were as follows:

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

SITI HAJAR BINTI OTHMAN

Date: 2 December 2011

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LIST OF SYMBOLS

a	Absorbance
A	Pre-exponential factor
c_p	Specific heat capacity
C	Concentration
C_o	Initial concentration
D	Diameter
E	Thermodynamic internal energy
E_a	Activation energy
f_A	Fraction of anatase crystal structure
G	Gibbs free energy
ΔG	Gibbs free energy difference
h	Enthalpy
hv	Photon energy
I	Unit tensor
I_A	X-ray intensities of the anatase (1 0 1) diffraction peak
I_R	X-ray intensities of the rutile (1 1 0) diffraction peak
$\boldsymbol{J}$	Diffusion flux of species
k	Rate constant
k_H	Heat conduction coefficient
K	Constant
M	Results obtained manually
M_w	Average molecular weight
P	Pressure

R	Gas constant
Re	Reynold numbers
-R	Without chemical reaction
+R	With chemical reaction
S	Results obtained from CFD simulation
SA	Surface area
T	Temperature
$\boldsymbol{v}$	Vector velocity
V_{avg}	Average velocity
Y	Mass fraction
β	Corrected band broadening
θ	Diffraction angle
λ	Wavelength
μ	Viscosity
ρ	Density
ρg	Gravitional body force
$\overline{\overline{\tau}}$	Stress tensor
Subscript $_j$	Species j

LIST OF ABBREVIATIONS

fwhm	Full width at half-maximum
i.e.p.	Isoelectric point
BET	Brunauer-Emmett-Teller
CFD	Computational fluid dynamics
CVD	Chemical vapour deposition
DDL	Diacetyldihydrolutidine
DRS	UV-vis diffuse reflectance spectrophotometer
EDX	Energy x-ray dispersive spectroscopy
EELS	Electron energy loss spectroscopy
FTIR	Fourier transform infrared
GRAS	Generally regarded as a safe material
HTC	Heat transfer coefficient
MOCVD	Metal organic chemical vapour deposition
PAA	Polyacrylic acid
SAXS	Small angle X-ray scattering
SEM	Scanning electron microscope
STEL	Short term exposure limit
TBOT	Titanium (IV) butoxide
TEM	Transmission electron microscope
TGA	Thermogravimetry
TTIP	Titanium isopropoxide
UV	Ultraviolet
XPS	X-ray photoelectron spectroscopy

XRD	X-ray diffraction

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