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Development of Cu/TiO_2 Photocatalyst for Hydrogen Production under Visible Light

By

Leong Siew Yoong

A THESIS
SUBMITTED TO THE POSTGRADUATE STUDIES PROGRAMME
AS A REQUIREMENT FOR THE
DEGREE OF MASTER OF SCIENCE
CHEMICAL ENGINEERING
BANDAR SERI ISKANDAR,
PERAK
MAY, 2009

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTP or other institutions.

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Name : LEONG SIEW YOONG

Date : ____

Acknowledgement

This dissertation was made possible by the help and support of many people. First of all, I would like to express my sincere gratitude and appreciation to my supervisor, Dr. Chong Fai Kait, for providing me with this unique research opportunity, and for her guidance and support all the way in my two years period of study and preparation of this thesis. Throughout my study and research project, she has constantly given me insightful advice. I have not only learnt from her but have also been inspired by her dedicated attitude to science. It has been a marvelous learning experience.

I would like to acknowledge all the staff members in the Chemical and Mechanical Engineering Department for their contributions to an active academic atmosphere. In addition, this research work was made possible by the generous financial support from the MOSTI (E-Science grant 03-02-02-SF0002).

Lastly, and most importantly, I felt very grateful to my parents for their unending support and love for the pursuit of my MSc. Thank you always for being there to support me.

ABSTRACT

Technologies for generating hydrogen from water using modified photocatalyst have drawn many attentions. In this study the photocatalysts for hydrogen generation were synthesized using two methods; complex-precipitation and wet impregnation method. Cu/TiO_2 with 2, 5, 10 and 15 wt% loading was prepared, dried and prior to calcination, thermal gravimetric analysis was carried out to determine their thermal stability. Based on the thermograms, the calcination temperature was estimated to be 300°C or higher. Therefore, the photocatalysts were calcined at 300°C, 400°C and 500°C for 30 min. The effect of transition metal loading and calcination temperatures on the photocatalytic activity was investigated. Photocatalytic activity was carried out under visible light illumination (500 W halogen lamp as the light source). The screening process is used to monitor the photocatalytic activities for hydrogen production in a multiport reactor containing of photocatalyst, water and methanol (as scavenger). The amount of hydrogen produced decrease as the calcination temperature increases for all the catalysts. The photocatalysts were also characterized using Temperature Programmed Reduction (TPR), Diffuse Reflectance UV-Vis (DR-UV-Vis), Field Emission Scanning Electron Microscope (FE-SEM), Fourier Transform Infared (FTIR), X-ray Difractometer (XRD) and surface area determination (BET). The results from TPR and XRD indicated that the only Cu species present was CuO supported on TiO_2. The SEM micrographs showed morphology of the prepared samples with particle size around 20 nm to 100 nm. The effect of transition metal loading was studied and found that incorporating with copper enhance the photocatalytic activity compared to TiO_2. However higher concentration of transition metal loading up to 15 wt% led to the decrement of the photocatalytic activity. The lower photocatalytic activity can be influence by the surface saturation of Cu which minimized the light penetration from reaching to the surface of the TiO_2. The incorporation of Cu transition metal had successfully shifted the TiO_2 band gap to a longer wavelength as evidence by DR-UV-Vis.

ABSTRAK

Teknologi untuk penghasilan hidrogen dari air dengan menggunakan modifikasi fotomangkin telahpun mendapat banyak perhatian. Fotomangkin Cu/TiO_2 yang telah disintesis menggunakan dua teknik iaitu pemendakan-kompleks dan impregnasi basah telah diaplikasikan dalam penyelidikan ini. Cu/TiO_2 dengan kandungan logam sebanyak 2, 5, 10 dan 15 wt% telah disediakan dan dikeringkan. Seterusnya, penentuan suhu penguraian menggunakan TGA yang dilakukan keatas fotomangkin segar sebelum meneruskan proses kalsinasi. Berdasarkan graf penguraian tersebut, suhu minimum bagi kalsinasi ialah 300°C dan ke atas. Seterusnya, fotomangkin dikalsin pada suhu 300°C, 400°C dan 500°C selama 30 min. Kegiatan fotoaktiviti untuk penghasilan hidrogen dijalankan di dalam multiport yang berisi fotomangkin, air dan metanol (sebagai bahan korban) di bawah sinaran lampu halogen 500 W sebagai sumber cahaya untuk semua fotomangkin. Kegiatan fotoaktiviti juga dijalankan tanpa menggunakan metanol sebagai eksperiment terkawal. Berdasarkan keputusan dari pengskrinan, fotoaktiviti optimum adalah bagi fotomangkin 10 wt% bagi kedua-dua kaedah. Pencirian fotomangkin Cu/TiO_2 ini telah dilakukan dengan menggunakan Penurunan Berprogramkan Suhu (TPR), Membaur Refleksi UV-Vis (DR-UV-Vis), Bidang Emisi Pengimbasan Elektron Mikroskop (FE-SEM), Fourier Transformasi Inframerah (FTIR), Pembelauan Sinar-X (XRD), teknik penjerapan fizik (BET) dan Analisa Terma Gravimetrik (TGA). Kesan penambahan kandungan Cu dan peningkatan suhu kalsinasi ke atas kegiatan fotoaktiviti tersebut disiasat. Fotoaktiviti penghasilan hidrogen bagi semua fotomangkin didapati menurun apabila suhu kalsinasi meningkat. Keputusan XRD yang diperolehi menunjukkan kehadiran spesis CuO sahaja. FE-SEM menunjukkan bahawa morfologi untuk butiran sampel adalah dalam julat sekitar 20 nm ke 100 nm. Kesan daripada penambahan Cu yang dikaji dan didapati bahawa aktiviti fotomangkin dipertingkatkan berbanding dengan TiO_2. Namun demikian, kandungan Cu yang berlebihan (15 wt%) mengakibatkan penurunan kegiatan fotomangkin. Penurunan fotoaktiviti disebabkan oleh kepekatan Cu yang terlalu tinggi dan seterusnya mengurangkan penembusan cahaya untuk sampai ke permukaan TiO_2. Penambahan Cu dari unsur peralihan menyebabkan pengurangan "band gap" berbanding dengan TiO_2 (3.2 eV) sepertimana yang telah

dibuktikan oleh DR-UV-Vis dan membolehkan fotomangkin yang telah dimodifikasi ini untuk menyerap lebih banyak cahaya tampak.

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W - Watt

$h\nu$ - Photon energy

e^- - electron

h^+ - hole

LIST OF ABBREVATIONS

TPR - Temperature Programmed Reduction
FTIR - Fourier Transform Infared
DR-UV-VIS - Diffuse Reflectance UV visible
FE-SEM - Field Emission Scanning Electron Microscope
XRD - X-ray Diffractometer
BET - Brunauer-Emmet-Teller
TGA - Thermal Gravimetric Analyzer
R&D - Research and Development
C.B - Conduction band
V.B - Valence band
SAA - Specific surface area
K - Kelvin
nm - nanometer
mA - mili Ampere
kV - kilo Volt
KM - Kubelka-Munk