

FAKULTI : FAKULTI KEJURUTERAAN KIMIA DAN KEJURUTERAAN TENAGA
TAJUK : PERBINCANGAN KEPUTUSAN PEMERIKSAAN SEMULA TESIS PELAJAR

BUTIRAN PELAJAR	KETERANGAN PELAJAR	ULASAN DAN TINDAKAN FAKULTI	KELULUSAN																														
NAMA : SAEED DELAVARI NO K/P @ ISID : 201001M10035 NO MATRIK : PK093053 PROGRAM : DOKTOR FALSAFAH (KEJURUTERAAN KIMIA) JENIS PENGAJIAN : PENYELIDIKAN BENTUK PENDAFTARAN : SEPENUH MASA PENYELIA : PROF. DR. AISHAH SAIDINA AMIN BIL SEM: 8 / 12 STATUS : PEPERIKSAAN MUKASURAT : 1/1	<table><tr><th>Bil.</th><th>Tarikh</th><th>Catatan</th></tr><tr><td>1.</td><td>13/8/2014</td><td>Pelajar Hantar Tesis untuk Peperiksaan</td></tr><tr><td>2.</td><td>16/11/2014</td><td>Viva Keputusan C tempoh 12 bulan</td></tr><tr><td>3.</td><td>7/7/2015</td><td>Terima Tesis untuk pemeriksaan semula</td></tr><tr><td>4.</td><td>8/7/2015</td><td>Tesis dihantar ke Pemeriksa Dalam dan Pemeriksa Luar</td></tr><tr><td>5.</td><td>30/11/2015</td><td>Pemeriksa Luar memberi Keputusan B1 – Semakan Penyelia</td></tr><tr><td>6.</td><td>28/12/2015</td><td>Pemeriksa Dalam memberi Keputusan B2 – Pembetulan 6 Bulan</td></tr><tr><td>7.</td><td>9/6/2016</td><td>Terima Tesis untuk semakan Pembetulan Pertama</td></tr><tr><td>8.</td><td>22/6/2016</td><td>Pemeriksa Dalam memberikan Keputusan Tidak Dianugerahkan Ijazah.</td></tr><tr><td>9.</td><td>23/6/2016</td><td>SPS memohon pengesahan dakwaan Laporan Pemeriksa Dalam ke Fakulti.</td></tr></table>	Bil.	Tarikh	Catatan	1.	13/8/2014	Pelajar Hantar Tesis untuk Peperiksaan	2.	16/11/2014	Viva Keputusan C tempoh 12 bulan	3.	7/7/2015	Terima Tesis untuk pemeriksaan semula	4.	8/7/2015	Tesis dihantar ke Pemeriksa Dalam dan Pemeriksa Luar	5.	30/11/2015	Pemeriksa Luar memberi Keputusan B1 – Semakan Penyelia	6.	28/12/2015	Pemeriksa Dalam memberi Keputusan B2 – Pembetulan 6 Bulan	7.	9/6/2016	Terima Tesis untuk semakan Pembetulan Pertama	8.	22/6/2016	Pemeriksa Dalam memberikan Keputusan Tidak Dianugerahkan Ijazah.	9.	23/6/2016	SPS memohon pengesahan dakwaan Laporan Pemeriksa Dalam ke Fakulti.	- SPS menerima maklum balas fakulti pada 15 Ogos 2016 melalui surat rasmi bertarikh 8 Ogos 2016. - Mesyuarat telah diadakan pada 2 Ogos bagi meneliti dan semakan pelaporan data dalam tesis pelajar yang dipengerusikan oleh Dekan, FKT dan 2 orang Panel Pakar dilantik daripada FS dan FKT. - Hasil Mesyuarat semua panel memutuskan supaya pelajar menyediakan data asal untuk semua gambarajah XRD (tesis muka surat 91), FTIR (tesis muka surat 148) dan XPS (tesis muka surat 151) dalam tesis. - Mesyuarat Japsu adalah dipohon untuk menentukan keputusan asal atau kedudukan pelajar dan tempoh pembetulan tesis melalui pengesahan dari Fakulti.	Setuju / Tidak Setuju Ulasan : _____ _____ _____ Tandatangan Dekan Sekolah Pengajian Siswazah & Cop Rasmi Tarikh : _____
Bil.	Tarikh	Catatan																															
1.	13/8/2014	Pelajar Hantar Tesis untuk Peperiksaan																															
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RUJUKAN KAMI:

UTM.J.46/14.14/1/6/3/15(246)

8 Ogos 2016

RUJUKAN TUAN:

Y. Bhg Prof. Dr. Zaidatun TasirDekan
Sekolah Pengajian Siswazah
Universiti Teknologi Malaysia
Johor Bahru, Johor

Assalamualaikum wrt wbt,

Y. Bhg Prof.

**SEGERA
DENGAN TANGAN***Untuk dibincangkan dan
menyempurnakan
[Signature]***SEMAKAN PELAPORAN DATA DALAM TESIS PELAJAR****Nama Pelajar : SAEED DELAVARI****Program: Doktor Falsafah (Kejuruteraan Kimia)**

Dengan hormatnya saya merujuk kepada perkara di atas.

2. Sukacita dimaklumkan bahawa fakulti telah mengadakan mesyuarat mengenai semakan pelaporan data dalam tesis pelajar (Saeed Delavari) pada 2 Ogos 2016 yang dihadiri oleh 2 orang panel (pakar) yang dilantik dari Fakulti Sains dan seorang panel (pakar) dari FKT dipengerusikan oleh Dekan, Fakulti Kejuruteraan Kimia dan Kejuruteraan Tenaga.

3. Hasil daripada mesyuarat tersebut, semua panel telah memutuskan supaya pelajar hendaklah menyediakan 3 data asal untuk semua gambarajah XRD, FTIR dan XPS seperti yang dinyatakan di bawah, iaitu seperti mana diperlukan oleh Pemeriksa Dalaman bagi membuktikan bahawa tiada salah laku data pada tesis pelajar tersebut. Disertakan juga petikan komen dari Pemeriksa Dalaman.

- i. XRD - rujuk *Figure 4.1* dan tesis mukasurat 91
Komen: *"..still did the same mistake by using incorrect figure.."*
- ii. FTIR - rujuk *Figure 5.4* dan tesis mukasurat 148
Komen: *"..the line of the FTIR spectra became smoother but still questionable.."*
- iii. XPS - rujuk *Figure 5.7(a), Figure 5.7(b)* dan tesis mukasurat 151
Komen: *"..cheating by using the figure that is not belong to his work.."*

Sehubungan itu, pihak fakulti memohon pertimbangan Y. Bhg Prof bagi menentukan kedudukan pelajar untuk diberi tempoh pembetulan tesis.

Sekian, terima kasih.

'Berkhidmat Untuk Negara Kerana Allah'

...2/-

Prof. Dr. Mohd Ghazali Bin Mohd Nawawi
 Prof. Madya Dr. Abdul Razak bin Rahmat
 Fakulti Kejuruteraan Kimia dan Kejuruteraan Tenaga

Melalui
 Dekan
 Fakulti Kejuruteraan Kimia dan Kejuruteraan Tenaga

Yg. Bhg Prof./Dr.,

NAMA PELAJAR : Saeed Delavari
PROGRAM : Doktor Falsafah (Kejuruteraan Kimia)
SEMAKAN PELAPORAN DATA DALAM TESIS PELAJAR

Perkara di atas dirujuk.

2. Untuk maklumat kronologi Peperiksaan Lisan Pelajar adalah seperti perincian berikut;

Tarikh	Kronologi
16 November 2014	Viva Keputusan C tempoh 12 bulan
7 Julai 2015	Terima tesis untuk pemeriksaan semula
8 Julai 2015	Tesis dihantar ke Pemeriksa Luar dan Pemeriksa Dalam
30 November 2015	Pemeriksa Luar memberi Keputusan B1 Semakan Penyelia
28 Disember 2015	Pemeriksa Dalam memberi Keputusan B2 Pembetulan 6 Bulan
9 Jun 2016	Terima tesis untuk Semakan Pembetulan Pertama
22 Jun 2016	Pemeriksa Dalam memberi keputusan Tidak Dianugerahkan Ijazah

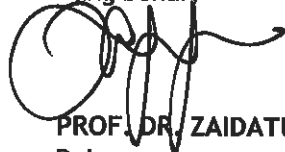
3. Seperti dibangkitkan dalam laporan pemeriksa, fakulti adalah dimohon membuat pengesahan dakwaan salah lapor data pada tesis pelajar. Sehubungan itu, pihak SPS memohon fakulti untuk melantik pakar bagi mengesahkan dakwaan ini.

4. Dilampirkan komen pemeriksa, cabutan tesis pelajar dan artikel jurnal yang dilampirkan oleh pemeriksa sebagai rujukan.

Sekian, kerjasama Yg. Bhg Prof./Dr. amat dihargai dan diucapkan terima kasih.

'Berkhidmat Untuk Negara Kerana Allah'

Yang benar,



PROF. DR. ZAIDATUN TASIR
 Dekan

Sekolah Pengajian Siswazah
 UTM, Skudai

☎ 07-5537881

✉ deansps@utm.my



UTM
UNIVERSITI TEKNOLOGI MALAYSIA

PENGESAHAN SEMAKAN PEMBETULAN TESIS
(CERTIFICATION ON THE CORRECTION OF THESIS)

Tarikh (Date): _____

Dekan
Sekolah Pengajian Siswazah
Universiti Teknologi Malaysia
81310 UTM Skudai
Johor

No. Faks: 07-5537800

Maklumat peperiksaan: (Diisi oleh SPS)

Tarikh viva (Date of viva):
16/11/2014

Tempoh pembetulan (Duration for correction):
c - tanpa reviva

Tuan (Dear Sir),

OTAJUK TESIS (Title of Thesis) (Diisi oleh SPS): **Photoreduction of Carbon Dioxide and Methane to Formate, Acetate Derivatives and Hydrogen Over Immobilized Titania Nanoparticles and Nitrogen-Doped Titania Nanotube Arrays**

NAMA PELAJAR (Name of Student) (Diisi oleh SPS): **Saeed Delavari**

FAKULTI (Faculty): **Fakulti Kejuruteraan Kimia dan Kejuruteraan Tenaga**

Semakan pembetulan: **Pertama /Kedua*** (Correction verification: **First/Second***) (Diisi oleh SPS)

1. Dengan ini saya mengesahkan telah menyemak dan meneliti dan berpuas hati bahawa pelajar:
(I hereby certify that I have read and verified the thesis and satisfied that the candidate):

(Initial)

telah membuat segala pembetulan dan mencapai tahap sebagaimana yang dicadangkan oleh panel pemeriksa dan saya mengesyorkan pelajar di atas dianugerah Ijazah Sarjana/Doktor Falsafah (has done all the necessary corrections recommended by the Panel of Examiners and I recommend that the candidate be awarded Master/Phd* degree)

sedikit pembetulan yang hanya perlu disahkan oleh penyelia dan saya mengesyorkan pelajar di atas dianugerah Ijazah Sarjana/Doktor Falsafah (minor corrections need to be verified by the supervisor and I recommend that the candidate be awarded Master/Phd* degree)

2. Pelajar gagal membuat pembetulan sebagaimana yang dicadangkan oleh panel pemeriksa (The candidate failed to carry out all the necessary corrections recommended by the Panel of Examiners)

i. membuat pembetulan semula (redo correction)

ii. Tempoh pembetulan (Duration for correction):hari/bulan*(days/months*).
Berikan perincian maklumat pembetulan yang dikhendaki (Please provide details for the corrections needed).

iii. tidak dianugerah Ijazah (not be awarded)

☒

3. Penyataan Lain (Other Remarks - if any): Pembetulan telah dibuat sebanyak dua kali. Untuk komen lanjut sila lihat lampiran.

Pengesahan dibuat oleh (Certified by):

Nama (Name): _____

Pemeriksa Luar/Pemeriksa Dalam*
(External Examiner/Internal Examiner)*

Alamat (Address):
PROFESSOR DR. AISHAH ABDUL JALIL
Department of Chemical Engineering
Faculty of Chemical and Energy Engineering
Universiti Teknologi Malaysia
81310 UTM Johor Bahru, Johor.

22/6/2016

Perhatian (Attention):

Boleh dihantar dengan faks (07-5537800) untuk kegunaan segera tetapi salinan asal **MESTI** dihantar ke Sekolah Pengajian Siswazah. (This certification may be faxed (07-5537800) for urgent usage but the original copy **MUST** be sent to the School of Graduate Studies).

* Sila potong yang tidak berkenaan (*Delete where not applicable)

Conclusion from Internal Examiner for Second-Correction for PhD Thesis of Saeed Delavari

Title: Photoreduction of Carbon Dioxide and Methane to Formate, Acetate Derivatives and Hydrogen Over Immobilized Titania Nanoparticles And Nitrogen-Doped Titania Nanotubes Arrays

Examiner : Prof. Dr Aishah Abdul Jalil (Internal)

The conclusion from internal examiner regarding to Saeed's response for each comments are as follows:

No.	Examiner Comment	Conclusion from Examiner	Remark (Latest thesis)
	The candidate should get the "real" figures for comments below.		
1.	Page 79 : Move the Fig. 3.4 into Chapter 4 (Result and Discussion).	OK.	Page 94
2.	Page 92: The JCPDS 84-1286 shown in Fig. 4.1 is wrong.	The student still did the same mistake by using the incorrect figure. Unfortunately, the student did not understand what the meaning of the JCPDS figure. This is really a ridiculous mistake because as a PhD student who is doing this kind of main analysis (XRD) in the catalyst area, he should know the exact figure. The reference for the answer of this question is attached, and many images could be also found from google image.	Page 91

3.	Page 149: Run and show the “real” FTIR spectra for Fig. 5.4.	In the 1st correction, the student sketched the FTIR spectra by himself (Page 149), which is a very disgraceful mistake as a PhD student. In this 2nd correction, the line of the FTIR spectra became smoother but still questionable. The reference for the nitrogen-doped TiO₂ is attached.	Page 148
4.	Check all the references in the thesis and make sure that they are appropriate for the related sentences.	OK.	
5.	Page 152: Show the appropriate XPS figure for the interaction between the TiO ₂ and Nitrogen.	The Figure 5.7b is not same with the Figure 5.7a. Thus, again the student also did the ridiculous cheating by using the figure that is not belong to his work. The references for the nitrogen-doped TiO₂ are also attached.	Page 151 
6.	Page 153: Delete the bullet in Fig 5.7.	OK.	
7.	Page 154: Combine the Fig. 4.3 and Fig. 5.8 to show the changes before and after doping with N. Make sure you get the “real” figure for all the figures.	OK.	Page 154

Kepada yang Berkenaan,

Komen umum dari saya:

Pada pendapat saya pelajar tidak layak dianugerahkan PhD dari UTM kerana sebab2 berikut:

- 1) Pelajar didapati menipu (plagiarism) dalam viva beliau, telah dikemukakan bukti yang sah iaitu paper yang beliau tiru dan diakui oleh panel viva semua tetapi pelajar masih tidak mengaku (sila rujuk komen pengerusi).
- 2) Viva terpaksa diberhentikan oleh pengerusi separuh jalan kerana pelajar banyak tidak dapat memberikan jawapan yang sepatutnya semasa viva.
- 3) Walupun demikian, kami para penilai dan pengerusi viva masih setuju untuk memberi peluang kedua kepada pelajar dengan memberi keputusan C kepada pelajar untuk membuat pembetulan. Akan tetapi, dalam 2nd correction ini, saya mendapati ada lagi data yang tidak jelas (tipu lagi). Saya sertakan beberapa bahan rujukan untuk pihak SPS rujuk kepada mereka yang lebih pakar dalam bidang pencirian bahan contohnya para pensyarah dari Fakulti Sains.

Oleh itu kesimpulan dari saya, pelajar telah banyak kali menipu data walaupun telah diberi peluang untuk membetulkannya, maka bagi saya beliau tidak layak dianugerahkan PhD demi menjaga kualiti penganugerahan PhD di UTM.

Sekian terima kasih.


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22/6/2016

Phase Characterization of TiO₂ Powder by XRD and TEM

Kheamrutai Thamaphat^{1*}, Pichet Limsuwan¹ and Boonlaer Ngotawornchai²

ABSTRACT

In this study, the commercial TiO₂ nanopowder and micropowder of anatase phase and rutile phase have been characterized by x-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD patterns of nano-TiO₂ in rutile and anatase phases exhibit broad peaks whereas both phases of micro-TiO₂ demonstrate very sharp peaks. TEM images show that the grain size of TiO₂ micropowders and TiO₂ nanopowders are 0.3-0.7 μ m and 10 nm, respectively. The selected-area electron diffraction patterns of TiO₂ nanopowders in rutile and anatase phases are consistent with XRD results.

Key words: TiO₂, anatase, rutile, micro and nanopowders, TEM, XRD

INTRODUCTION

Titanium dioxide or titania (TiO₂) was first produced commercially in 1923. It is obtained from a variety of ores. The bulk material of TiO₂ is widely nominated for three main phases of rutile, anatase and brookite (Kim *et al.*, 2005). Among them, the TiO₂ exists mostly as rutile and anatase phases which both of them have the tetragonal structures. However, rutile is a high-temperature stable phase and has an optical energy band gap of 3.0 eV (415 nm), anatase is formed at a lower temperature with an optical energy band gap of 3.2 eV (380 nm) and refractive index of 2.3 (Brady, 1971).

TiO₂ is mainly applied as pigments, adsorbents, catalyst supports, filters, coatings, photoconductors, and dielectric materials. In recent years, TiO₂ has been well known as a semiconductor with photocatalytic activities and has a great potential for applications such as environmental purification, decomposition of

carbonic acid gas, and generation of hydrogen gas (Zhang *et al.*, 2000). In most of these cases, the size of the TiO₂ particles is an important factor affecting the performance of the materials. It is not surprising; therefore, that much research has been focused upon the reduction of the particle size. Much effort has been devoted to the preparation of TiO₂ nanopowders, including sol-gel route, homogeneous precipitation, hydrothermal methods, flame synthesis and relatively new molten salts method (Bilik and Plesch, 2007). They were usually found that different routes often produced different results. Even for the same route, using different amount of the starting materials, the obtained powder size is different (Li *et al.*, 2002).

Consequently, phase and particle size are the important parameters that influence physical properties of material. Several techniques could be used for the investigation of them. However, the particle size determination can be based on direct observation of particles by transmission

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electron microscopy (TEM) or scanning electron microscope techniques, in this case, we can also receive the important information on the shape of particles. Data on particle size can be obtained by X-ray diffraction (XRD) technique as the particle size is related to the diffraction peak broadening. It is important to note that TEM and XRD methods allow not only to measure the particle size, but also to identify crystalline phases.

MATERIALS AND METHODS

Four commercial TiO_2 samples used in this experiment were provided by Aldrich: (i) 99.7 % anatase, nanopowder; (ii) 99.8 % anatase, micropowder; (iii) 99.5 % rutile, nanopowder; (iv) 99.9 % rutile, micropowder.

XRD measurements were performed on the Bruker D8 Advance diffractometer operating in the reflection mode with $\text{Cu-K}\alpha$ radiation (35 kV, 30 mA) and diffracted beam monochromator, using a step scan mode with the step of 0.075° (2θ) and 4 s per step. Diffraction patterns of both anatase and rutile TiO_2 powders were compared with reference to JCPDS database. Additionally, the morphology of the powder was observed by

TEM with a JEOL JEM-2100 ultra high resolution TEM operating at 160 kV.

RESULTS AND DISCUSSION

XRD

XRD patterns of nano- TiO_2 and micro- TiO_2 in rutile and anatase phases are shown in Figure 1 and Figure 2, respectively. In Figure 1, XRD patterns exhibited strong diffraction peaks at 27° , 36° and 55° indicating TiO_2 in the rutile phase. On the other hand, in Figure 2, XRD patterns exhibited strong diffraction peaks at 25° and 48° indicating TiO_2 in the anatase phase. All peaks are in good agreement with the standard spectrum (JCPDS no.: 88-1175 and 84-1286). From Figure 1 and Figure 2, they were shown that the diffraction pattern peak intensity of the TiO_2 increases with increasing particles size. These results suggested that the nano- TiO_2 powder is composed of irregular polycrystalline. Amorphous revealed a broad pattern with low intensity; however, the effect of the amorphous materials on the broadening of the XRD patterns of nanosized TiO_2 is negligible.

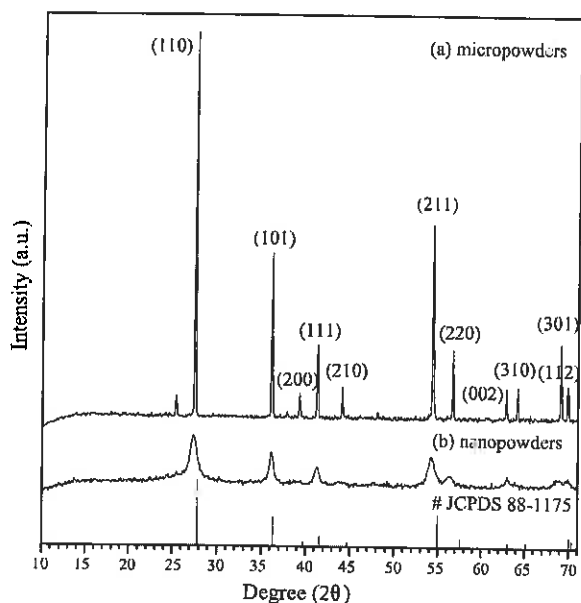


Figure 1 X-ray diffraction of rutile TiO_2 (a) micropowders and (b) nanopowders.

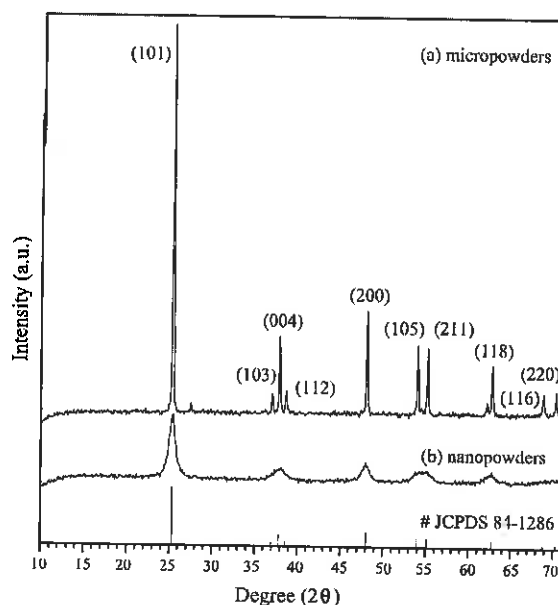


Figure 2 X-ray diffraction of anatase TiO_2 (a) micropowders and (b) nanopowders.

TEM

TEM was used to further examine the particle size, crystallinity and morphology of samples. TEM bright field images of TiO_2 micropowders in rutile and anatase phases are shown in Figure (3a) and (4a), respectively. It is clearly seen that the TiO_2 powders in rutile phase consist of both spherical and rod shapes but the particle of TiO_2 powders in anatase phase are mostly spherical morphology. Furthermore, it can be estimated that the particle size of samples in Figure (3a) and (4a) are microscale with the grain size about 0.3-0.7 μm .

TEM bright field images of TiO_2 nanopowders in rutile and anatase phases are shown in Figure (3b) and (4b), respectively. It can be estimated that the particle size of powders in Figure (3b) and (4b) are nanoscale with the grain size less than 10 nm. The corresponding selected-area electron diffraction (SAED) patterns of nano- TiO_2 powders in rutile and anatase phases are shown in Figure (3c) and (4c), respectively. These are in agreement with XRD results in Figure (1b) and (2b), respectively. In Figure (3c), the SAED patterns of nano- TiO_2 powders in rutile phase shows spotty ring patterns without any additional

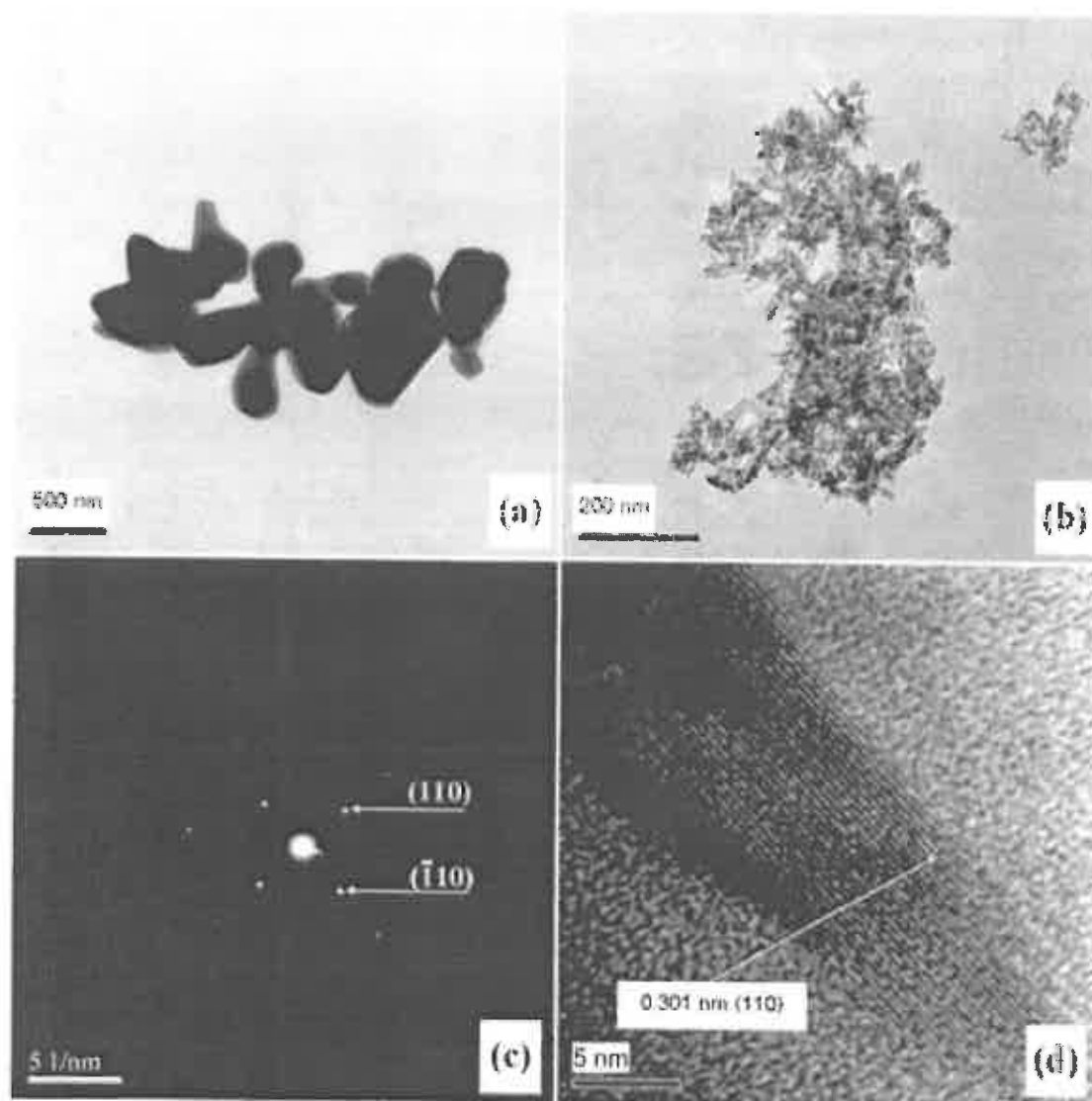


Figure 3 Images of rutile phase. (a) TEM image of micro- TiO_2 powder; (b) TEM image of nano- TiO_2 powder; (c) SAED pattern of nano- TiO_2 powder and (d) HRTEM image of nano- TiO_2 powder.

diffraction spots and rings of second phases, revealing their well crystalline. On the other hand, the SAED patterns of nano-TiO₂ powders in anatase phase (Figure 4c) shows that the brightness and intensity of polymorphic ring is weak, so they are poorly crystallized and partly amorphous.

The crystallinity of nano-TiO₂ powders can also be observed by phase-contrast images or Moire patterns. Figure (3d) and (4d) show crystal lattice planes of nano-TiO₂ in rutile and anatase phases, respectively. It is seen that, for rutile phase,

only one crystal lattice plane(110) with d-spacing of 0.301 nm is obtained, whereas those of anatase give many crystal lattice planes with d-spacing of 0.313 nm for the plane (101).

CONCLUSION

In this work, a study has been carried out on the identification of phase and particle size of TiO₂ powders using XRD and TEM techniques. All high purities samples were commercial TiO₂. From the results, X-ray diffraction patterns can

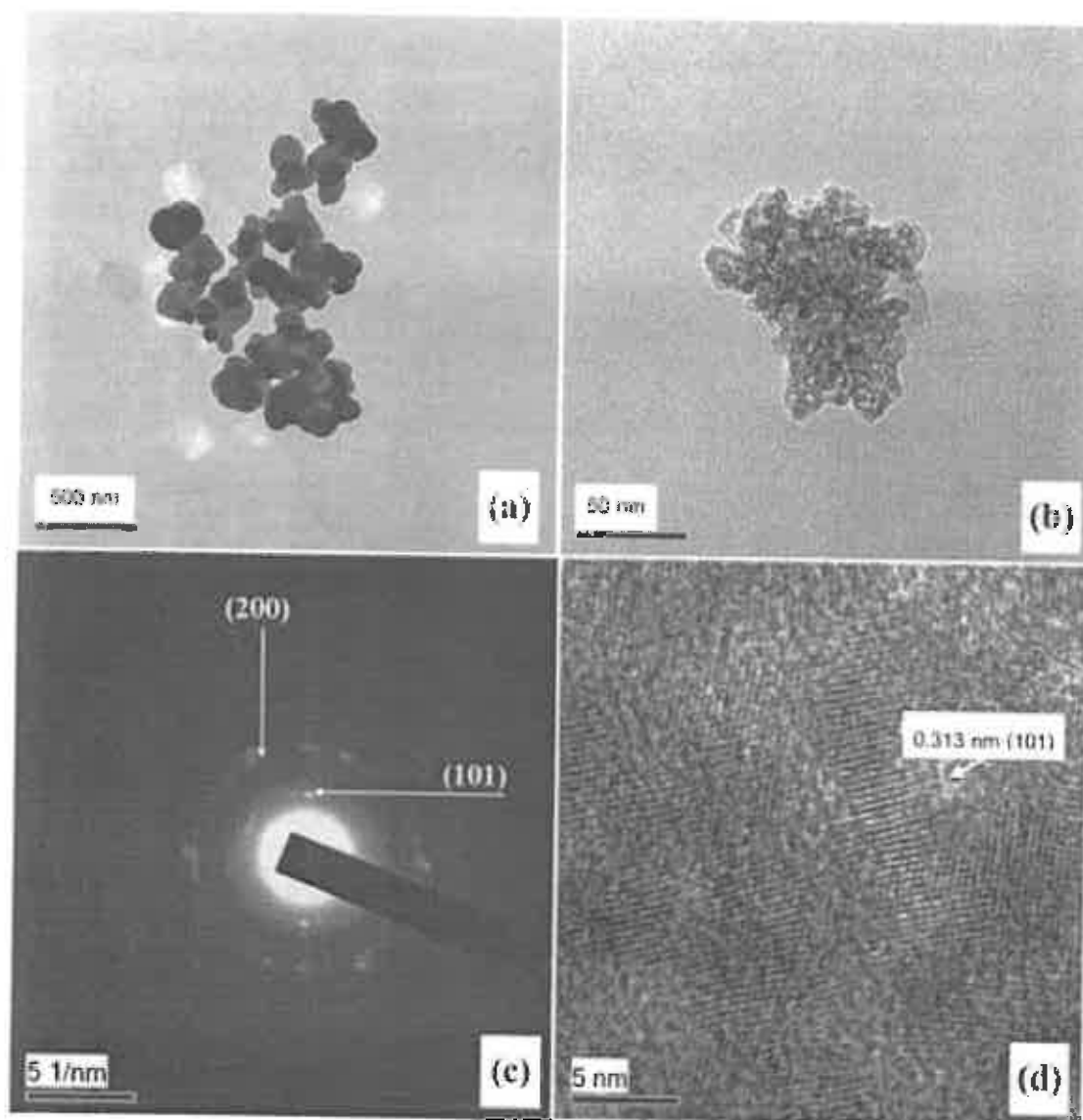


Figure 4 Images of anatase phase. (a) TEM image of micro-TiO₂ powder; (b) TEM image of nano-TiO₂ powder; (c) SAED pattern of nano-TiO₂ powder and (d) HRTEM image of nano-TiO₂ powder.

confirm the TiO_2 phases. Furthermore, the particle size can be clearly indicated by characteristic of XRD pattern; the diffraction pattern peak intensity of the TiO_2 increases with increasing particles size. Additionally, TEM was used to further examine the crystallite/particle size, the crystallinity and morphology of samples. TiO_2 powders in rutile phase consist of both spherical and rod shape; on the contrary, the particle of TiO_2 in anatase phase has mostly spherical morphology.

ACKNOWLEDGEMENTS

This work is financially supported by the Department of Physics, the Faculty of Science, King Mongkut's University of Technology Thonburi and the Nano Technology Center (NANOTEC).

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Dynamic photocatalytic reduction of CO₂ to CO in a honeycomb monolith reactor loaded with Cu and N doped TiO₂ nanocatalysts



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Continuous operation

ABSTRACT

Cordierite honeycomb monoliths loaded with N/TiO₂ and Cu/TiO₂ nanocatalysts for dynamic photocatalytic CO₂ reduction with H₂ to CO in a continuous photoreactor illuminated with UV-light irradiations have been investigated. The nanocatalysts, loaded over the monoliths channels using sol-gel dip-coating method, were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), N₂ adsorption-desorption, X-ray photoelectron spectroscopy (XPS), UV-vis diffuse reflectance and photoluminescence (PL) analysis. Crystalline and anatase TiO₂ structure with nanoparticles evenly supported over the cordierite monolith channels were observed. Cu and N presented over TiO₂, shifted band gap energy towards visible region and hindered charges recombination rate. Loading Cu and N greatly improved TiO₂ photoactivity for dynamic CO₂ reduction to CO. Due to high photoactivity and selectivity, Cu/TiO₂ assisted system yielded 14 times higher CO than the N/TiO₂ and 64 times the amount of copper observed over pure TiO₂ in a continuous operation of photoreactor. This significant improvement in Cu/TiO₂ activity was noticeable due to efficient trapping and transport of electrons by Cu-metal. With unique properties, N/TiO₂ showed good activity for continuous CO₂ reduction to CH₄. In addition, a photocatalytic reaction mechanism is proposed to understand the experimental results over Cu and N modified TiO₂ catalysts in a continuous operation of photoreactor.

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1. Introduction

The rise in atmospheric CO₂ concentration due to fossil fuel combustion is causing major concerns of energy sustainability and environmental protection [1]. Numerous efforts are devoted to CO₂ capture, storage and utilization; yet photocatalytic CO₂ transformation to fuels provides one prospective path for the storage of solar energy to chemical energy [2,3]. During the recent decades, photocatalytic CO₂ reduction to carbon monoxide [4], methane [5], methanol [5] and hydrocarbons [6] over different types of semiconductor materials has been consistently drawing increasing attention. The state-of-the-art photocatalytic CO₂ reduction, however, requires photocatalysts that meet certain stringent criteria [7–9].

Most of the research on CO₂ photoreduction has been related to TiO₂ due to its numerous advantages which include low cost, avail-

able in excess, nontoxic, chemically/thermally stable and strong oxidative potential [10,11]. However, TiO₂ is active only under UV-light due to its wide band gap energy (~3.2 eV for anatase). The shorter lifetime of photo-generated electron-hole pairs in TiO₂ is another challenge, resulting in lower photoactivity. Different noble metals such as Au, Ag, Cu, Ni, and Pt are considered efficient to improve TiO₂ photoactivity and selectivity [12–15]. The noble metals serve as electron traps to suppress the recombination rate of the photo-generated charges. Among all, copper has been reported as an efficient dopant to enhance TiO₂ photoactivity for selective CO₂ reduction [16–19]. Incorporating Cu-metal ions (Cu⁰, Cu⁺, Cu²⁺) into TiO₂ could lead to stimulate electron transfer between metal/semiconductor junction to improve photoactivity [20]. In addition, copper has low price, non-toxicity, environmental acceptability and good photoactivity [21].

Non-metallic elements such as C, S, F and N are considering as economical dopants to improve TiO₂ photoactivity. However, special considerations were paid for N since it has particular doping property and visible light sensitivity. In different studies, it has been reported that N shifted TiO₂ band gap energy for efficient CO₂ reduction to fuels under visible light irradiations [22,23]. However, there is a lack of systematic study about the function of N/TiO₂

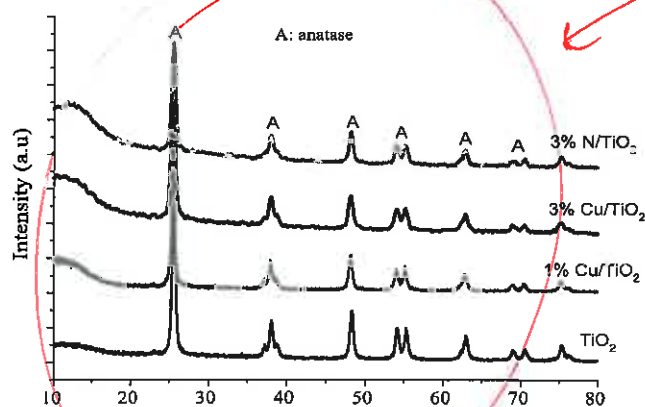
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Table 1

Summary of physicochemical characteristics and products analysis over various catalysts.

Sample	BET (m ² /g)	Pore volume (cm ³ /g)	Crystal size ^a (nm)	E _g ^b (eV)	Yield rate ^c (μmole g-catal. ⁻¹ h ⁻¹)		Selectivity ^d (%)		Quantum yield ^e (%)
					CO	CH ₄	CO	CH ₄	
TiO ₂	42	0.13	19	3.12	12	0.46	96.31	3.69	0.0013
3% N/TiO ₂	47	0.15	14	3.06	56	2.15	96.30	3.70	0.0061
3% Cu/TiO ₂	50	0.18	13	3.02	763	4.20	99.45	0.55	0.0826

^a Crystal size calculated using Scherrer equation based on 101 peak of TiO₂.^b Band gap energy calculated using Tauc equation, from a plot of (αhν)² versus photon energy (hν).^c Yield rate of C_i (μmole g-catalyst⁻¹ h⁻¹) = $\frac{\mu\text{mole of } C_i \text{ produced}}{(\text{wt. of catalyst} \times \text{time})} \times 100$.^d Selectivity of product C_i (%) = $\frac{\text{moles of } C_i \text{ in product}}{\text{Total moles of } C \text{ produced}} \times 100$.^e Quantum yield of CO (%) = $\frac{2 \times \text{mole of CO production rate (mole/s)}}{\text{mole of photons intensity (mole/s)}} \times 100$.Fig. 1. XRD patterns of pure TiO₂, Cu/TiO₂ and N/TiO₂ samples.

under UV-light irradiations. It is important to make clear the role of N in TiO₂ for CO₂ photoreduction under UV and visible light irradiations. Besides, there are limited reports up to date on dynamic and selective CO₂ photoreduction with H₂ to CO; therefore, it is noteworthy to explore Cu and N doped TiO₂ catalysts.

On the other hand, if the exposed surface area of catalyst is lower and if the photons are not effectively distributed over the photocatalyst than the system efficiency will be lowered [24,25]. During the past years, slurry photoreactors in liquid phase are the most used in CO₂ reduction, but they have poor light penetration in the suspension [26]. In addition, it is very difficult to achieve uniform light distribution over the entire catalyst surface in slurry systems, which is critical to activate photocatalyst [27]. Due to the complex nature of photocatalytic reactions, the efficient interaction between light irradiation, reactants and catalyst is one of the major challenges in the design of photoreactors. The catalyst support is efficient only if it has a high ratio of active surface area to reactor volume, efficient light distribution and greater photonic efficiency [28].

Presently, gas phase and in particular structured photocatalytic systems has been suggested for many photocatalytic processes [29]. Among the structured supports, monolithic substrates are exploited for many industrial processes due to unique structure with high surface area to volume ratio, thus could increase interaction between light irradiation and catalyst. We have recently reported gas phase photocatalytic CO₂ reduction in a batch mode monolith photoreactor, where Au-In/TiO₂ [30] and Ni-In/TiO₂ [31] photocatalysts were immobilized on the monolith channels. With this new configuration, enhanced yield rate, improved selectivity and high photonic efficiency were attained.

In this study, dynamic photocatalytic CO₂ reduction with H₂ to CO over Cu/TiO₂ and N/TiO₂ nanocatalysts loaded on cordierite honeycomb monoliths in a continuous photoreactor operation has been investigated. The effects of Cu and N on the photocatalytic

also different with Saeed XRD used the same although they are catalyst (same lab)

properties of TiO₂ based structured systems for selective CO₂ reduction via reverse water gas shift (RWGS) reaction under UV light irradiation are discussed in detail. The quantum yield and reaction pathways were analyzed to elucidate the role of each metal in the CO₂ reduction process.

2. Experimental

2.1. Photocatalyst preparation

Cordierite honeycomb monoliths (100 cells per square inch, cylindrical in shape) measuring 20 mm in length and 60 mm diameter purchased from China were used. The nanocatalysts were prepared and supported over the monolith channels using modified sol-gel method as reported previously [3]. In a typical procedure, 15 mL acetic acid (1 M) was added dropwise to an aqueous solution of 20 mL titanium tetra isopropoxide (Ti(C₃H₇O)₄) in 60 mL isopropanol (C₃H₇O). The obtained mixture was stirred at ambient temperature for 12 h to get titanium sol. Next, an adequate amount of copper nitrate or urea dissolved in deionized water was added to titanium sol and then aged for another 6 h to get clear sol. The sol obtained was poured into a glass container for coating over the monolith channels.

Before catalyst loading, monoliths were washed with acetone and isopropanol to remove any organic material, dried at 80 °C for 12 h and then cooled to room temperature. The initial weight of the dried monolith was noted and then dipped into the titanium sol to a specific time for the catalyst coating. The excess sol was blown off using hot compressed air. The coating procedure was repeated to reach an expected catalyst loading. The honeycomb monoliths were finally calcined at 500 °C for 5 h (5 °C min⁻¹). The amount of catalyst loaded was calculated by subtracting the final weight of catalyst coated monolith from the initial weight of bare monolith. For every coating, three readings were noted and their average values are reported.

2.2. Catalyst characterization

The crystalline phase was investigated using powder x-ray diffraction (XRD). The XRD patterns were collected between 10–80° of 2θ with a step size 0.05° and a step time of 1 s using a Bruker D8 advance diffractometer equipped with Cu- Kα incident radiation (λ = 1.54 Å, 40 kV and 40 mA). The morphology of the samples was examined by field emission scanning electron microscopy (FESEM, Hitachi SU8020). The elemental states were analyzed using X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD Shimadzu). The XPS spectrum was calibrated with respect to the binding energy of the C1s signal at 284.60 eV as the internal standard. The surface area measurements (BET) of the photocatalyst powders were carried out using N₂ adsorption-desorption isotherms with Surfer-

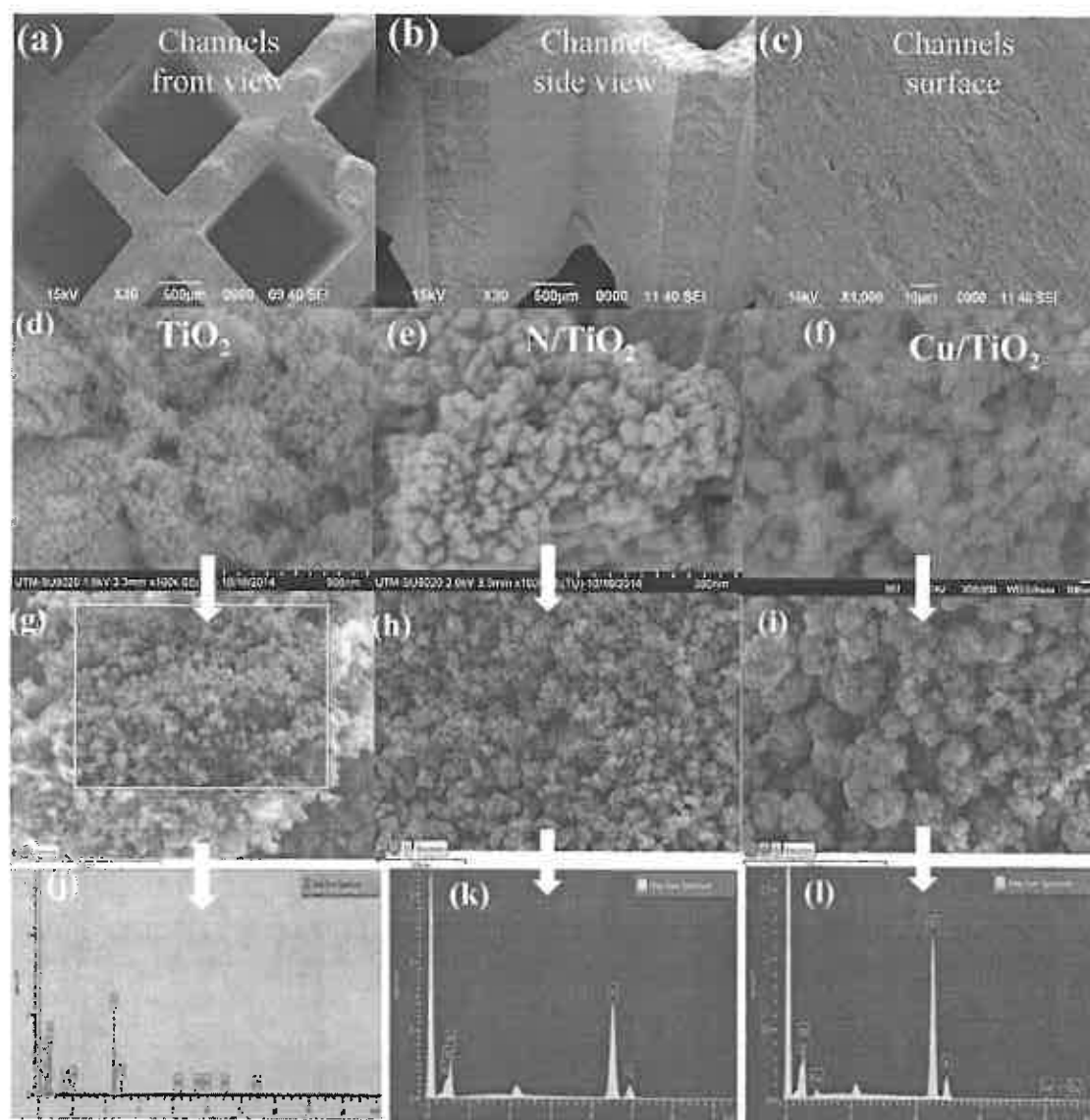


Fig. 2. SEM and FESEM images of cordierite honeycomb substrate loaded with catalyst nanoparticles: (a–c) SEM images of top and side view of catalyst loaded cordierite honeycomb channels, (d–f) FESEM images of TiO_2 , N/TiO_2 and Cu/TiO_2 nanoparticles, (g–i) elemental mapping of TiO_2 , N/TiO_2 and Cu/TiO_2 samples, (j–l) EDX plots of TiO_2 , N/TiO_2 and Cu/TiO_2 nanoparticles.

Thermo-Scientific after degassing at 250 °C for 4 h. UV–vis diffuse reflectance absorbance spectra were determined in the wavelength range of 200–800 nm using UV–vis spectrophotometer (Agilent, Cary 100) equipped with an integrated sphere. The charges recombination rate was analyzed using PerkinElmer LS 55 Luminescence Spectrometer.

2.3. Photocatalytic activity testing

The design of continuous monolith photoreactor used in this work was described in detail in our previous work [29]. The reactor was consisted of a stainless steel cylindrical vessel with a total volume 150 cm³, equipped with a quartz window and a reflector lamp located above the reactor. The catalyst coated cordierite honeycomb monoliths (100CPSI, L = 20 mm, d = 60 mm) were inserted inside the reactor chamber. 200 W Hg reflector lamp was used as a source of light with a maximum light intensity of 150 mW cm^{−2} and wavelength 254 nm. An optical process monitor ILT OPM-1D

and a SED008/W sensor was used to measure the light intensity. The reactor was purged using helium (He) flow before gas mixtures (CO_2 and H_2 , purity = 99.99%) was continuously passed through the reactor at a flow rate of 20 mL/min. The operating conditions used were CO_2/H_2 feed ratio 1.0, temperature 100 °C and pressure 1 atm. All the experiments were carried out in a continuous mode of operation and products were analyzed after regular intervals.

The CO_2 reduction products were analyzed using an on-line gas chromatograph (GC-Agilent Technologies 6890 N, USA) equipped with TCD and FID detectors. FID detector was connected with a HP-PLOT Q capillary column (Agilent, length 30 m, ID 0.53 mm, film 40 μm) for separation of C_1 – C_6 paraffin and olefins hydrocarbons, alcohols and oxygenated compounds. The TCD detector was connected to UCW982, DC-200, Porapak Q and Mol Sieve 13X columns. Porapak Q and DC-200 columns were used for separation of C_1 – C_5 compounds and light gasses (H_2 , O_2 , N_2 , CO) were separated using MS-13X columns.

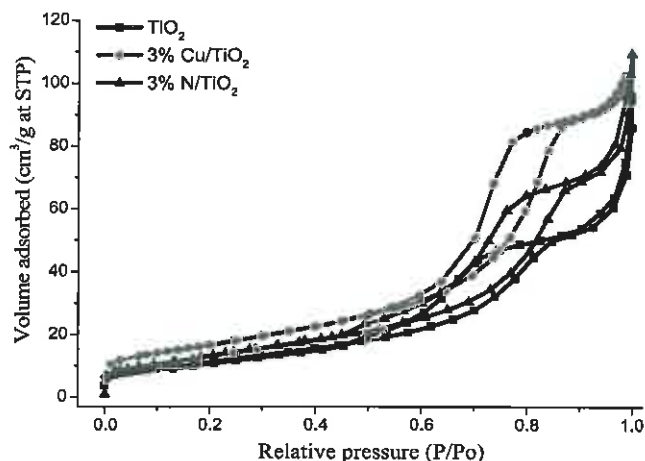


Fig. 3. N_2 adsorption-desorption isotherms of TiO_2 , N/TiO_2 and Cu/TiO_2 samples.

3. Results and discussion

3.1. Nanocatalysts characterization

XRD patterns of TiO_2 , Cu/TiO_2 and N/TiO_2 samples are presented in Fig. 1. Pure crystalline and anatase phase TiO_2 could be seen in all

the TiO_2 samples. All the peaks of TiO_2 and Cu/N loaded TiO_2 samples were identical, thus shift in peaks were not observed. The peaks attributable to Cu or N in metal or oxide states were not detected, possibly due to the low amount, or they were uniformly distributed inside the TiO_2 structure [32,33]. The crystallite sizes were estimated from the XRD patterns using Scherrer equation and the data is presented in Table 1. The TiO_2 crystallite size was gradually reduced with Cu and N loading. This was probably Cu and N presented over the TiO_2 structure prohibited crystal growth, resulting in reduced crystallite sizes [4,32].

The morphology of cordierite support, catalyst particles, and metals distribution is presented in Fig. 2. SEM micrographs in Fig. 2(a–c) depict catalyst deposited evenly over the cordierite surface with no broken layer. The sol-gel dip-coating method used to support catalyst over the monolith channels resulted in a good dispersion of catalysts over the cordierite surface. The mesoporous and uniform nanoparticles of TiO_2 , N/TiO_2 and Cu/TiO_2 could be seen in Fig. 2(d–f), respectively. Fig. 2(g–i) shows the elemental mapping images of pure TiO_2 , N/TiO_2 and Cu/TiO_2 samples. Noticeably, N and Cu metals, evenly distributed over the TiO_2 surface, can provide more active sites for the reactants. The EDX plots in Fig. 2(k–l) further confirmed the presence of N and Cu metals in TiO_2 .

The N_2 adsorption-desorption tests were performed to determine the surface area, pore volume and pore width of the catalysts. The isotherms of TiO_2 , N/TiO_2 and Cu/TiO_2 samples are illustrated in Fig. 3. Evidently, all the samples exhibited typical type IV isotherms

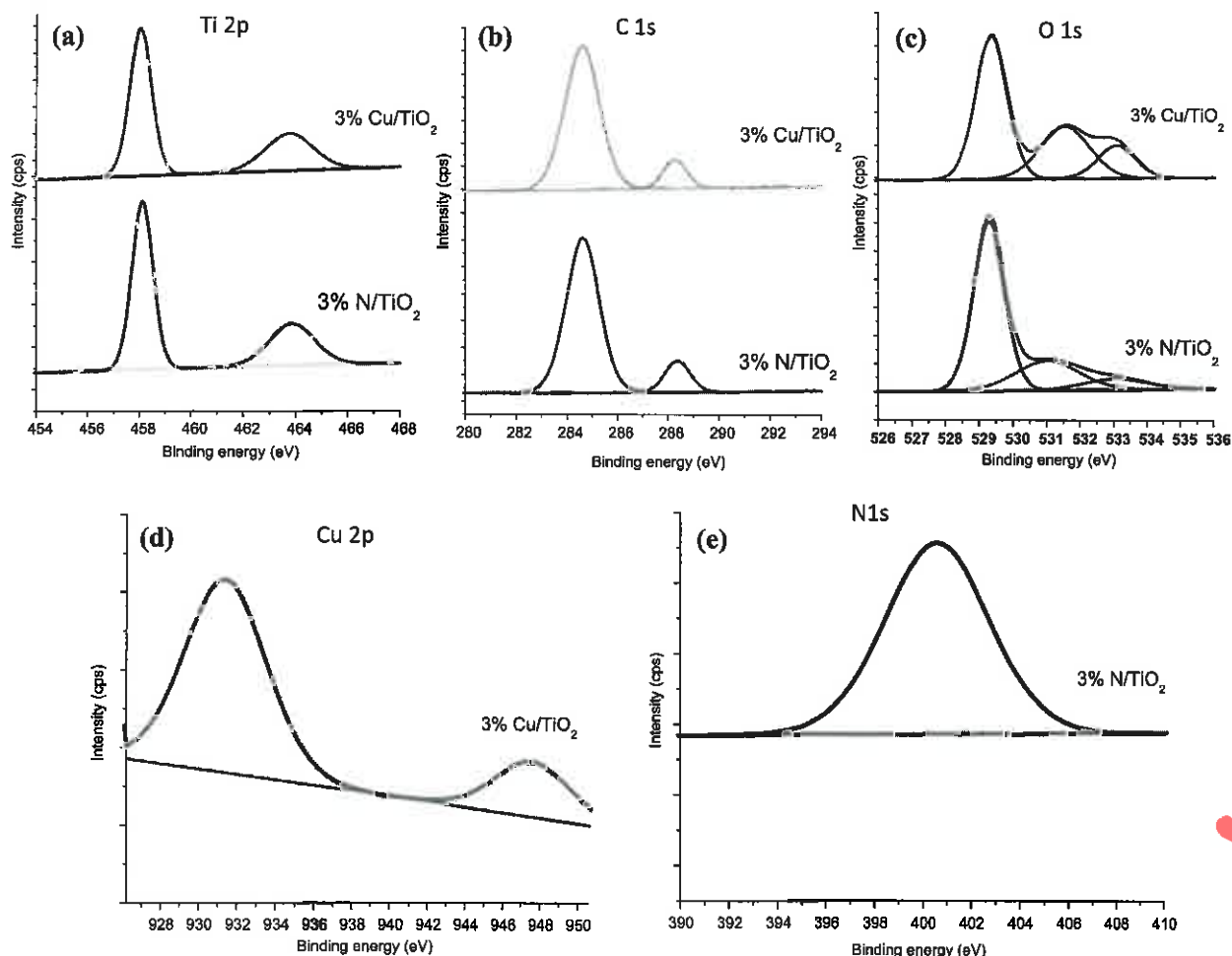


Fig. 4. XPS spectra of 3% N/TiO_2 and 3% Cu/TiO_2 samples: (a) $Ti\ 2p$ spectra of N/TiO_2 and Cu/TiO_2 , (b–c) $O\ 1s$ and $C\ 1s$ spectra of N/TiO_2 and Cu/TiO_2 samples, (d) $Cu\ 2p$ spectra of Cu/TiO_2 and (e) $N\ 1s$ spectra of N/TiO_2 .

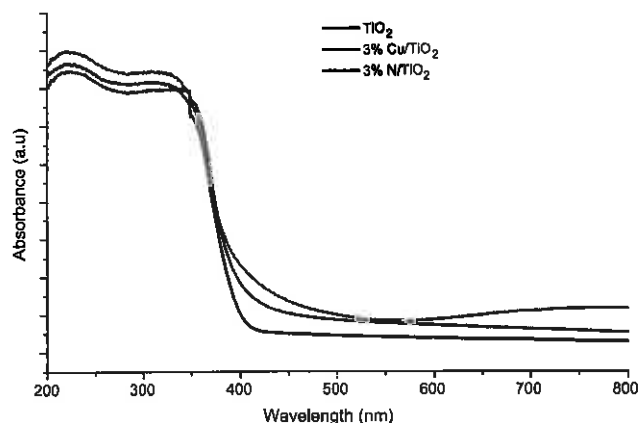


Fig. 5. UV-vis diffuse reflectance absorbance spectra of TiO_2 and doped TiO_2 samples.

with an increase in the volume of gas uptake. The hysteresis loops observed in all the samples, indicating mesoporous pore structure of TiO_2 . Suggestively, capillary and condensation reflections were observed in the TiO_2 sample, while the similar trends appeared in the N and Cu doped TiO_2 samples. BET surface area was measured from N_2 adsorption-desorption isotherms and the results are listed in Table 1. The BET surface area of TiO_2 was 42 increased to 47 and $50 \text{ m}^2/\text{g}$ in N/TiO_2 and Cu/TiO_2 samples, respectively. It is noticeable to see there is no significant effect on TiO_2 surface area by loading Cu and N metals. However, pore volume gradually increased with Cu and N loading.

X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation state of Ti, and chemical states of the component elements in 3 wt.% N/TiO_2 and 3 wt.% Cu/TiO_2 samples as presented in Fig. 4. The $\text{Ti } 2p_{3/2}$ and $\text{Ti } 2p_{1/2}$ binding energies (BE) in Fig. 4(a) attributed to the presence of titanium as Ti^{4+} oxidation state in both N/TiO_2 and Cu/TiO_2 samples. Fig. 4(b) shows spectra of O1s for the N/TiO_2 and Cu/TiO_2 samples. The XPS spectrum of O1s in N/TiO_2 reveals a peak with main components, one at 529.37 eV, characteristics of lattice oxygen (O^{2-}) and a high bending energy component at 531.57 and 533.11 eV related to metal-OH bond or free hydroxyl group (OH) on the surface. The same kind of analysis fitting can be determined for Cu/TiO_2 sample. The C1s peaks for N/TiO_2 and Cu/TiO_2 samples are presented in Fig. 4(c). The main peak at 284.60 eV is assigned to C-C and C-H hydrocarbon bonds. The peak at 288.31 eV can be attributed to carbon atoms bound to oxygen with double bond C=O. The relative concentration of peak at 284.60 eV was much more and may be recognized as the carbon from carbon tap used for sample analysis. Fig. 4(d) shows the spectra of Cu 2p peaks for Cu/TiO_2 with BE regions centered at $\sim 931.41 \text{ eV}$ ($2p_{3/2}$) and 947.48 eV ($2p_{1/2}$), respectively, indicating copper as Cu^{2+} or copper oxide (CuO) [34]. Fig. 4(e) shows spectrum of N/TiO_2 contains N 1s peak at approximately 400 eV, which reflects a chemical structure like O-Ti-N [2].

Fig. 5 shows UV-vis diffuse reflectance absorbance spectra of pure TiO_2 , N/TiO_2 and Cu/TiO_2 catalysts. The addition of N and Cu can obviously enhance the absorbance of TiO_2 under visible light irradiations. The band gap energy was measured from a plot of $(\alpha h\nu)^2$ versus $(h\nu)$ using the direct method and the results are presented in Table 1. The band gap energy of TiO_2 shifted towards the visible region by doping with Cu and N which is in good agreement with previous reports [23,35].

The photoluminescence (PL) spectra of TiO_2 , N/TiO_2 and Cu/TiO_2 samples are displayed in Fig. 6. The fluorescence peaks of TiO_2 and doped TiO_2 samples were in the range of 450–550 nm excited at wavelength 350 nm. The pure TiO_2 and doped TiO_2 peaks exhibited

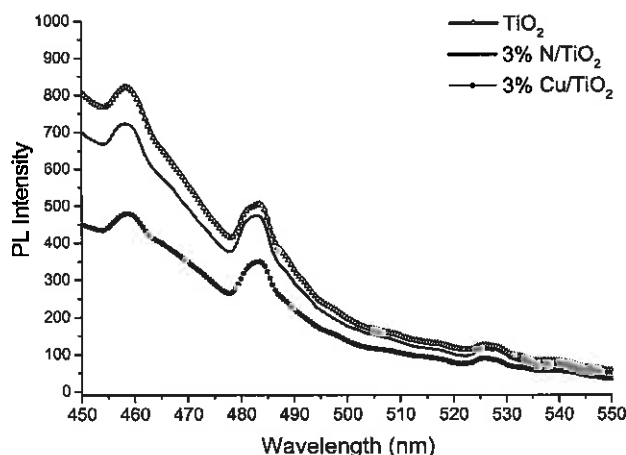


Fig. 6. Photoluminescence (PL) emission spectra of TiO_2 and Cu/N doped TiO_2 samples under the excitation wavelength of 350 nm.

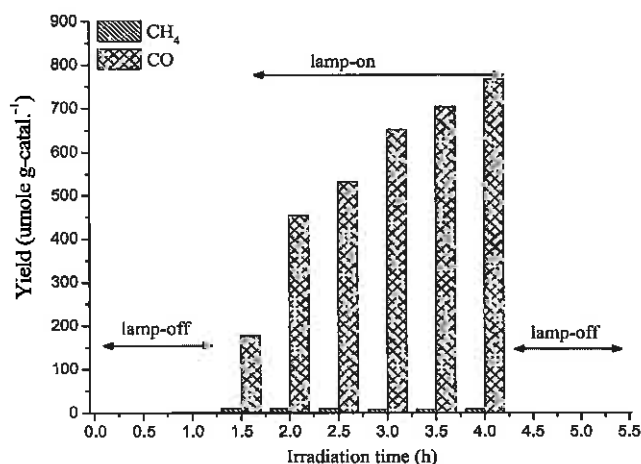


Fig. 7. Preliminary analysis of cordierite honeycomb loaded photocatalyst for CO_2 reduction with H_2 to CO and CH_4 under the lamp off and on condition in a continuous operation of photoreactor.

wide and strong PL signals in the identical regions. The existence of PL attributed to the recombination of e^-/h^+ pairs. In N/TiO_2 , lower PL intensities compare to pure TiO_2 , confirming hindered charges recombination rates by N. However, a significant decrease in PL intensity detected in Cu/TiO_2 sample probably Cu traps more electrons, thus prevents efficient charges recombination rate compared to N/TiO_2 and pure TiO_2 samples. Thus, it is anticipated that Cu would be more efficient than N to enhance TiO_2 photoactivity.

3.2. Photocatalytic CO_2 reduction with H_2

The control experiments were conducted for CO_2 reduction with H_2 under UV light irradiation at 100°C , CO_2/H_2 ratio 1.0 and feed flow rate $20 \text{ mL}/\text{min}$. In all the experiments carbon containing compounds were not detected in the reaction system when the lamp was off as shown in Fig. 7. However, a continuous CO and CH_4 production could be seen under light irradiation. This confirmed that the catalysts and monoliths were cleaned while carbon containing compounds were produced from CO_2 reduction only.

The effect of N-doping into TiO_2 photoactivity for CO_2 photoreduction with H_2 to CO and CH_4 under UV-light irradiation in a continuous monolith photoreactor is depicted in Fig. 8(a). CO was detected as the major CO_2 reduction product with a smaller

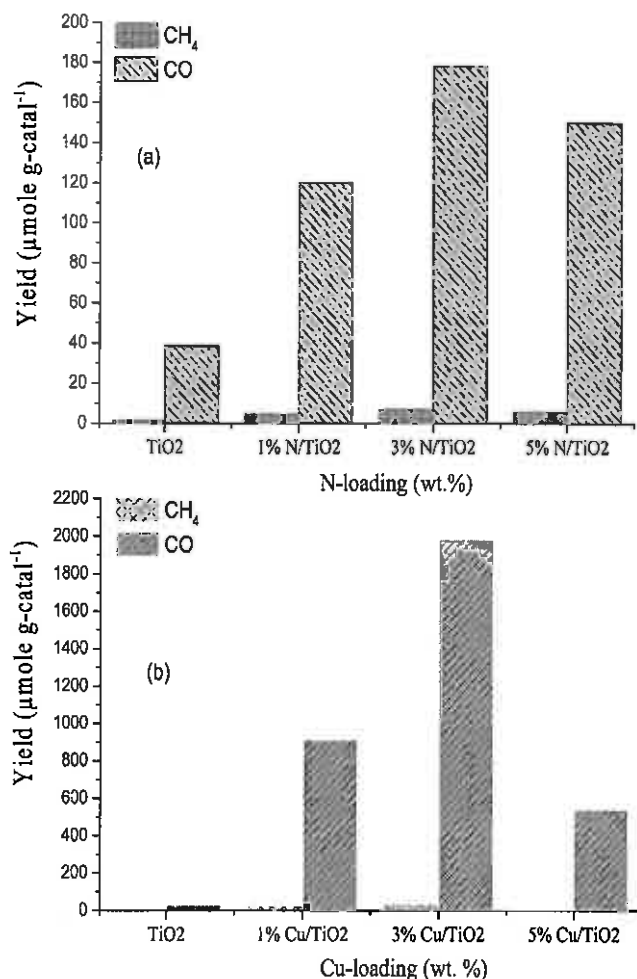


Fig. 8. Effect of N and Cu loading on TiO₂ photoactivity for dynamic CO₂ reduction to CO and CH₄ in a continuous operation photoreactor at CO₂/H₂ ratio 1.0 and feed flow rate 20 mL/min; (a) effect of N-loading, (b) effect of Cu-loading.

amount of CH₄ over both un-doped TiO₂ and N/TiO₂ samples. Pure TiO₂ scarcely reduced CO₂ and showed very poor activity for CO formation, but loading N enhanced CO production rate. The CO evolution increased remarkably with increasing N-doping up to an optimum and then gradually decreased. The large quantity of N-doping would result in more defect sites resulting in decreased photocatalytic activity [23]. Owing to the overall effects of defect sites, 3 wt.% N is an optimum amount to achieve the best photocatalytic activity in the present system.

Fig. 8(b) shows the effect of different amounts of Cu-loading (1 wt.%, 3 wt.% and 5 wt.% Cu contents) on the TiO₂ photoactivity for dynamic CO₂ conversion with H₂ under UV light irradiation. In all the cases, CO was the main product during CO₂ photoreduction with the smaller amount of CH₄. Noticeably, Cu-loading can increase CO₂ reduction efficiency for both CO and CH₄ production. In the presence of a small amount of Cu-content (1 wt.%), the photoactivity of TiO₂ was obviously enhanced. The activity of TiO₂ sample was further improved with increasing Cu-loading to 3 wt.% and the amount of CO detected was 1981 $\mu\text{mole g-catal}^{-1}\text{h}^{-1}$. This yield of CO production was higher than that of pure TiO₂ by more than 99 times. When Cu-loading was more than 5 wt.%, a reduction of photoactivity was observed. This was probably due to loading of excess Cu over the TiO₂ surface (shielding effect), causing a decrease of TiO₂ surface active sites or perhaps due to recombination centers over the TiO₂ surface [4,32]. Therefore, 3 wt.%

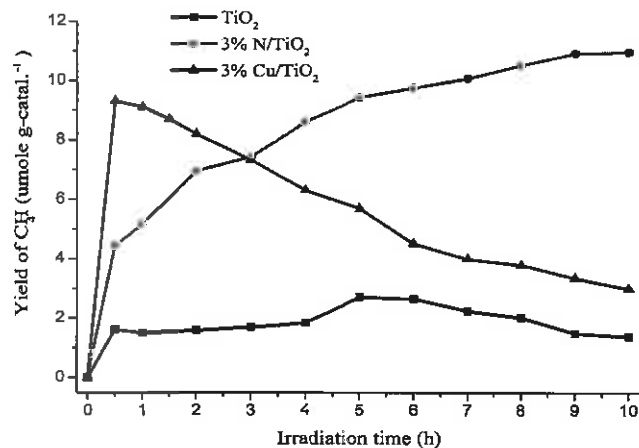


Fig. 9. Effect of irradiation time on CO₂ photoreduction with H₂ to CH₄ over TiO₂ and doped TiO₂ catalysts in continuous monolith photoreactor at CO₂/H₂ ratio 1.0 and the feed flow rate 20 mL/min.

Cu/TiO₂ has the highest activity over which maximum CO yield observed, considerably more than the amount of CO produced over N/TiO₂ and TiO₂ catalysts. This enhancement in the Cu/TiO₂ activity for CO production was probably due to the higher mobility of charges with hindered recombination rate by Cu-metal in monolith microchannels. Hence, Cu-metal has more ability to trap electrons as evidenced by PL analysis and due to the reduction potential difference of Cu/TiO₂ system, resulting in enhanced productivity [3].

Further investigations were carried out to study the effect of irradiation time on dynamic photocatalytic CO₂ reduction in a continuous photoreactor operation. Fig. 9 presents a dynamic CH₄ production over Cu/TiO₂ and N/TiO₂ catalysts at different irradiation time. Noticeably, Cu and N metals have different effects on CH₄ production. Increasing formation of CH₄ was observed over the N/TiO₂ catalyst during the entire irradiation time. CH₄ formation over Cu/TiO₂ presented a different behavior, initially reaching maximum concentration, and then gradually decreased. The decreased in CH₄ production over the irradiation time was possibly due to oxidation of CH₄ with O₂ to CO₂ in the presence of an efficient Cu/TiO₂ monolithic catalyst [36]. On the other hand, N enables trapping holes, resulting in a continual increase in the yield rate of CH₄. This also revealed prolonged stability and efficiency of N/TiO₂ catalyst for dynamic CH₄ production in a continuous operation of photoreactor [23].

Previously, it has been reported that both Cu and N doped TiO₂ photocatalysts could enhance CH₄ photo-generation over the irradiation time. We investigated continuous CH₄ and hydrocarbon production over a Cu-In/TiO₂ catalyst in a batch mode operation of monolith photoreactor under UV-light irradiation [4]. Liu et al. [37] reported increased in CH₄ yield rate with the irradiation time using Cu/TiO₂ catalysts in a slurry type photoreactor system. However, in the current study, different trends in CH₄ production over the cordierite honeycombs were perhaps due to gas phase reaction in a continuous monolith photoreactor operation. Similarly, Li et al. [23] observed CH₄ evolution rate increased with the irradiation time over N/TiO₂ during gas phase CO₂ reduction in a batch photoreactor under visible light irradiation. In this case CH₄ production trends are similar to current results, confirming N loading helps to produce CH₄ both in the gas phase and continuous operation of photoreactor. This also confirms higher stability and activity of N/TiO₂ for dynamic CH₄ production.

The yield of CO production during CO₂ reduction over TiO₂ and doped TiO₂ samples at different irradiation times is presented in

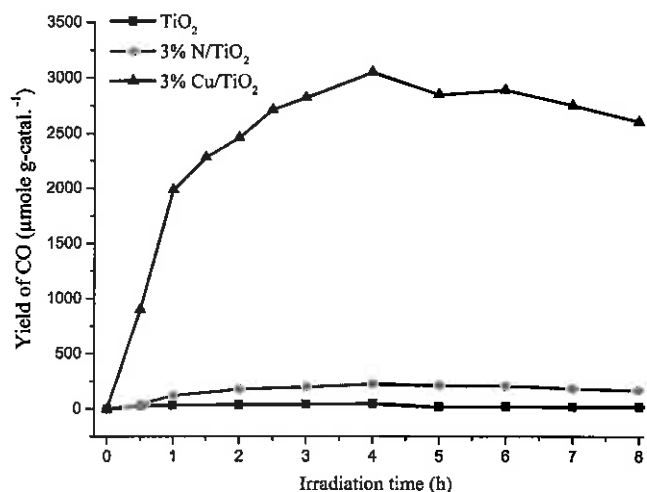


Fig. 10. Production of CO during CO₂ reduction with H₂ over TiO₂ and modified TiO₂ samples in continuous monolith photoreactor at CO₂/H₂ ratio 1.0 and the feed flow rate 20 mL/min.

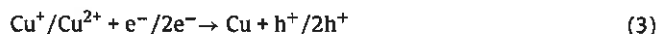
Fig. 10. Initially, the yield of CO production is much faster, but gradually decreased after 4 h of irradiation time. However, the amount of CO over a Cu/TiO₂ monolithic catalyst was significantly higher than N/TiO₂ and pure TiO₂. The much higher photoactivity for CO production confirms the potential of CO₂ reduction with H₂ in a continuous operation of photoreactor loaded with Cu/TiO₂ nanoparticles. However, the CO production rate was gradually decreased at a prolonged irradiation time due to oxidation of CO to CO₂ in the presence of O₂ or perhaps due to deteriorating catalysts photoactivity in the course of continuous CO₂ reduction over the irradiation time [31,36].

Table 1 summarizes yield rates and selectivity of different products over TiO₂ and doped TiO₂ catalysts. The main products observed were CO and CH₄ over TiO₂ and doped TiO₂ monolithic catalysts. However, in the case of Cu/TiO₂, smaller amount of hydrocarbons namely C₂H₄, C₂H₆, C₃H₆ and C₃H₈ were also detected in the gas mixture. The performance of Cu/TiO₂ was found to be the highest, giving a dynamic CO yield rate of 763 μmole g-catal.⁻¹ h⁻¹ a 14 fold more efficient than N/TiO₂ and 64 times more CO production over copper than un-doped TiO₂ catalyst. The selectivity of CO production over TiO₂ and N/TiO₂ were much closer (96%) but increased to 99% in Cu/TiO₂ catalyst. However, the production of CO as the main product over Cu/TiO₂ and N/TiO₂ was due to thermodynamic reduction potential difference between TiO₂ (−0.5 eV) and CO₂/CO (−0.48 eV) [2].

Photocatalytic CO₂ reduction by H₂ via reverse water gas shift (RWGS) reaction also contributed to CO production. Recently, it has been reported that CO₂ was firstly converted to CO and then transformed to CH₄ over TiO₂ based photocatalysts [38,39]. However, in the present study, due to continuous operation of photoreactor and efficient adsorption-desorption process inside monolith microchannels, CO was dynamically removed from the reactor over the irradiation time. Previously, we have investigated photocatalytic CO₂ reduction to CO over different co-doped TiO₂ nanocatalysts in a batch mode of monolith photoreactor. [40,31,29–41]. Therefore, it can be established that CO would be a major CO₂ reduction product via RWGS reaction in a monolith photoreactor operated in a batch or continuous mode of operation.

From Table 1, it is obvious that surface area, crystal size and band gap energy of Cu/TiO₂ and N/TiO₂ are much closer to each other. The higher Cu/TiO₂ photoactivity could not be linked to surface area or band gap energy. Therefore, enhanced Cu/TiO₂ photoactivity could

be due to higher mobility of electrons in Cu-doped TiO₂ samples as illustrated in Eqs. (1)–(3) [4,42].



The generation of Cu ions takes place through the oxidation of Cu metal by photo-generated holes (Eq. (1)). Due to rapid transfer of excited electrons to the Cu particles, e[−]/h⁺ pair's separation is enhanced as illustrated in Eqs. (2) and (3). Therefore, role of Cu in CO₂ reduction over Cu/TiO₂ is noticeable. As a consequence, higher photoactivity could be seen over Cu/TiO₂ monolithic photocatalyst for CO production. Recently, similar observations have been reported for photocatalytic CO₂ reduction to CO and CH₄ over Cu/TiO₂ photocatalyst in a gas phase system [43].

In order to investigate the performance of CO₂ photoreduction with H₂ over Cu and N doped TiO₂ photocatalysts in a continuous monolith photoreactor, the results are compared with the work reported by various researchers. N/TiO₂ catalyst was used for CH₃OH production and yield rate of 23 μmole g-catal.⁻¹ h⁻¹ was measured using a batch mode photoreactor [22]. CO₂ reduction with H₂O to CO was reported over g-C₃N₄-N-TiO₂ in batch mode operation with a maximum yield of 14.73 μmole after 12 h irradiation time [44]. Over I/TiO₂ and Cu-I/TiO₂, a CO yield rate of 3.9 and 12 μmole g-catal.⁻¹ was reported after 3.5 h during gas phase CO₂ reduction in a batch mode operation [20]. Similarly, photocatalytic CO₂ reduction with H₂O to CH₄ over different photocatalysts such as CH₄ yield of 100.22 ppm cm⁻² h⁻¹ over MgO/TNTs [45], 17 μmole g-catal.⁻¹ of CH₄ yield after 7 h over Ca₁₀Ti₁₀O₃ [46], rGO-Pt/TNTs with CH₄ yield rate of 10.96 μmole m⁻² [13], CH₄ yield rate of 23.10 μmole g-catal.⁻¹ after 480 min over 3-D Au/TiO₂ nanoparticles [47] and a CH₄ production of 184 μmole g-catal.⁻¹ after 24 h over Zn-Cu promoted TiO₂ has been reported by various researchers [38]. A comparison study between previous reports and current study revealed that monolith geometry facilitated in improving the photoactivity and selectivity of photocatalysts. Therefore, the role of cordierite honeycomb monolith loaded with Cu and N is obvious for dynamic CO production in continuous photoreactor operation. This is perceptibly due to a larger illuminated surface area with higher photon energy consumption inside the monolith channels [39].

The performance of cordierite honeycomb support loaded with Cu and N metals was further examined based on the quantum yield, calculated for each experiment, as the ratio of the product rate (mole per s) with photonic flux (mole per s). The quantum yield of CO₂ photoreduction to CO can be defined as the ratio of production rate (mole per s) with photonic flux (mole per s) as shown in Eq. (4) [48].

Quantum yield of CO(%)

$$= \frac{2 \times \text{moles of CO production rate (mol/sec)}}{\text{moles of photon flux (mol/sec)}} \times 100 \quad (4)$$

The quantum yield was calculated based on the CO production rate and moles of photon input energy over the catalyst surface as presented in Table 1. The quantum yield for dynamic CO production over cordierite honeycomb monoliths loaded with Cu/TiO₂ was greatly enhanced (0.083%) than N/TiO₂ and TiO₂ samples. Liou et al. [26] reported quantum efficiency of 0.012% and 0.057% for methanol and acetaldehyde, respectively, during photocatalytic CO₂ reduction with H₂O over NiO/InTaO₂ catalysts in an internally illuminated continuous monolith photoreactor. Obviously, higher quantum yield in the current study was due to a larger illuminated surface area because of monolith microchannels and using H₂ as a reductant.

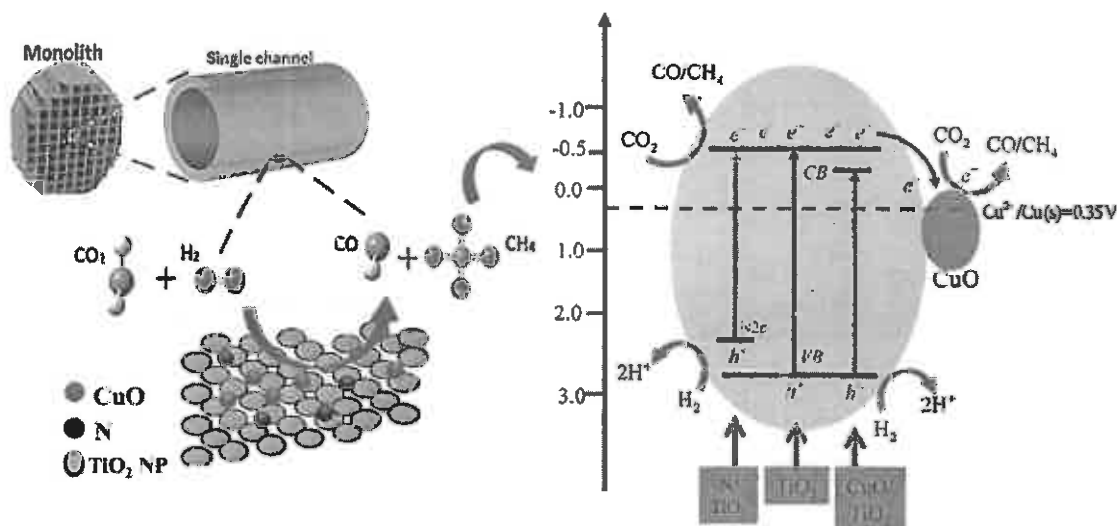


Fig. 11. Schematic of photocatalytic CO₂ reduction with H₂ over cordierite honeycomb loaded Cu/TiO₂ and N/TiO₂ catalysts.

3.3. Reaction mechanism

In the photocatalytic CO₂ reduction process, photo-generated electrons (e⁻) and holes (h⁺) involve in breaking O—C—O and H—H bonds with the formation of C—O and C—H bonds. The reaction mechanism was studied to get insight of CO₂ photoreduction over Cu/TiO₂ and N/TiO₂ catalysts. The electron-hole pairs separation and production of CO and CH₄ are illustrated in Eqs. (5)–(10) [42,43,49].



As the photocatalytic activity is closely related to the band structure of photocatalysts, separation and transportation of photo-generated carriers (i.e., electrons and holes) as well as the redox potential, the enhanced photocatalytic mechanism can be explained by the scheme presented in Fig. 11 [43,50]. Under the light irradiations, VB electrons of TiO₂ excited to CB creating holes in VB. Without metals-loading, these charges recombine back and only a fraction of electrons and holes participate in reduction and oxidation process, thus, TiO₂ shows a quite low photocatalytic activity. When Cu metal was loaded on TiO₂ surface, the CB electron of TiO₂ can transfer to these metals which cause electron-hole pair separation (Eq. (5)). Furthermore, more electrons could be trapped if the metal reduction potential is more positive than the CB of TiO₂. As the redox value of Cu is lower (+0.35) than the CB of TiO₂ (−0.50 V), thus electron can effectively be transferred to copper to prolong their lifetime [4,51,52]. H₂ molecules were dissociated to H⁺ ions while CO₂ reduced to CO and hydrocarbons by accepting the trapped electrons and H⁺ ions as explained in Eqs. (7)–(10). Some previous works have reported that all of the N/TiO₂ contributed to the visible light absorption by creating a new N 2p state slightly above the valence band of TiO₂ [23]. As to the current N/TiO₂ photocatalyst, upon UV-light irradiation, holes may be trapped by N to react with CO to produce CH₄.

The expressively enhanced in CO yield rate over Cu/TiO₂ was clearly due to higher trapping and mobility of electrons by Cu metal for CO₂ reduction inside monolith channels. On the other hand, continuous production of CH₄ over N/TiO₂ was perhaps due to adsorbed CO converted to CH₄ over N/TiO₂ in the presence of holes. In general, dynamic CO₂ conversion to CO and CH₄ at a higher yield rate was due to using cordierite honeycomb monolith support loaded with doped TiO₂ nanoparticles.

4. Conclusions

In this study, cordierite honeycombs loaded Cu/TiO₂ and N/TiO₂ nanocatalysts were developed for dynamic photocatalytic CO₂ conversion with H₂ under UV-light irradiation in a continuous operation monolith photoreactor. CO was the major CO₂ reduction product with a smaller amount of CH₄ over Cu and N/TiO₂ catalysts. Cu could improve TiO₂ photocatalytic activity by trapping electrons while N prolonged the lifetime of photo-generated charges by trapping holes. N-loading also promoted the formation of CH₄ during dynamic CO₂ reduction. The performance of Cu/TiO₂ was found to be the highest, giving a CO yield rate of 763 μmole g⁻¹ h⁻¹ a 14 fold more efficient than N/TiO₂ and 64 times more than un-doped TiO₂ catalyst. The photoactivity of Cu and N/TiO₂ samples gradually reduced after 4 h of irradiation time. However, N/TiO₂ found very stable for CH₄ production over the entire irradiation time. In summary, by means of Cu and N doping, highest efficiency for dynamic CO₂ conversion was obtained due to a larger illuminated surface area, higher photon energy and better charges separation inside monolith microchannels. Both Cu and N are equally important to exert a substantial impact on the enhancement of CO and CH₄ production. This development confirmed a high performance of cordierite honeycomb monolith loaded with Cu/TiO₂ than N/TiO₂ for dynamic CO₂ conversion to fuels.

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Highly efficient visible-light photocatalyst of nitrogen-doped TiO₂ nanoparticles sensitized by hematoporphyrin



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ABSTRACT

A novel hybrid nanocomposite based on N-doped TiO₂ nanoparticles was prepared and sensitized with hematoporphyrin for visible light utilization. The product was characterized by thermogravimetric analysis (TGA), differential thermal analysis (DTA), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), BET surface area analysis, UV-vis spectroscopy and field emission scanning electron microscopy (FE-SEM). The results showed that the N-doped TiO₂ has smaller crystalline size and larger specific surface area than bare TiO₂ particles. Surface oxygen defects, produced by nitrogen doping, would improve the advantage of hematoporphyrin placement and then facile electron exciting and transferring to the conduction band of N-doped TiO₂. The crystal structure of N-doped TiO₂ was not affected by the sensitizing; however, the surface area was significantly increased. Application of the hybrid nanocomposite exhibited higher visible-light absorption leading to an enhancement of about 1.7 and 4.2 times in photocatalytic degradation of methyl orange compared with N-doped TiO₂ and just bare TiO₂ utilization, respectively. The photocatalytic degradation of methyl orange with the products was demonstrated to follow first order kinetic model. The produced nanocomposite can be reused at least four times recycling without significant loss of activity.

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1. Introduction

Today, the presence of injurious organic pollutants in wastewater has caused serious environmental problems and thereupon purification of contaminated water is one fascinating challenge [1]. Accordingly, use of renewable energy has become an interesting research area because of its sustainability and positive effect on environment and the limited utilization of fossil fuels [2,3]. Solar energy, because of its great availability, its cleanliness as well as easy operation and use, has become the first choice in the field of renewable energy sources [4,5].

Another matter of interest is utilizing efficient and selective metal oxide semiconductors in the process of the photocatalytic degradation of organic pollutants [6,7]. A well-known semiconductor is TiO₂ with excellent photocatalytic properties that make it highly valuable for the oxidation of organic pollutants. It is a superior photocatalyst for both purification of water and air due to its nontoxicity, long-term stability, inexpensiveness and chemical stability over a wide pH range and also in a large number of solvents [8,9].

One problem with pure TiO₂ nanoparticle is its large band gap energy that can be activated under UV light irradiation. However, this situation limits its application under direct solar light, as UV light accounts for only a small fraction (<5%) of the solar spectra compared to visible region (45%) [10]. In order to eliminate this drawback and enhance the visible region absorption of TiO₂, different approaches have been proposed in the literature. Since the discovery of activity of nitrogen-doped TiO₂ under visible light irradiation by Asahi et al. [11], great attention has been given to doping TiO₂ by nitrogen atom [12–15]. Insertion of N atom produces a localized energy state above the valence band of TiO₂, thus when N doped TiO₂ is exposed to visible light, electrons are transferred from these localized states to the conduction band [16]. Compared to the other non-metal dopants (S, P and C), N-doped TiO₂ materials represent a considerable photocatalytic activity and strong absorption under visible light irradiation [17,18]. Evidently, the mechanism of nitrogen doping to increase the visible-light absorption and photocatalytic activity of TiO₂ is different from that of dye sensitization. It is therefore, concluded that coupling of nitrogen doping with dye sensitization is a good way to significantly improve the visible-light absorption and photocatalytic activity of TiO₂.

The sensitization of TiO₂ by dyes such as ruthenium polypyridyl complexes [19], squaraines [20], porphyrins [21] and natural dyes [22] has been widely used for achieving desired electronic and

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optical properties. As a surface modification technology, dye sensitization can solve two major drawbacks of ultrafast recombination of photogenerated electron–hole pairs and a low quantum yield [5]. Highly efficient dye sensitizers should meet the following needs: (i) a wide range of absorption spectrum, intense substrate adsorption capacity efficiency; (ii) high quantum yield and excited states with long lifetime; and (iii) matching band structure to decline energy loss during the process of electron transfer [23–25]. Porphyrin and porphyrin derivatives, because of their strong light absorption in the region of 400–450 nm (Soret band), as well as 500–700 nm (Q band), are appropriate candidates for sensitizing different structures of TiO_2 semiconductors. One of porphyrin derivatives, hematoporphyrin (HP), is of natural origin derived from acid extraction of blood. The chemical structure of HP is similar to chlorophyll and the “hem” of hemoglobin, that are well known in nature [26]. HP consists of very large conjugated double bonds of tetrapyrrole, this extended conjugation leads to strong absorption of the visible spectrum with a thermal and photochemical stability. In this case, the sensitizer dye molecules bonded on the surface of TiO_2 can be excited by visible light and then the photoinduced electrons transfer into the conduction band (CB) of TiO_2 is facilitated. While CB injected electron reacts with acceptor molecules, i.e. with dissolved oxygen in solutions around TiO_2 surface and forming $\text{O}_2^{\cdot-}$ and $\text{HO}^{\cdot}$; the valence band (VB) remains unaffected [27,28]. The use of HP has been reported to meet the requirements relating to cost efficiency, non-toxicity and complete biodegradation.

In the present investigation, we present a novel hybrid nanocomposite, produced from N-doped TiO_2 nanoparticles and hematoporphyrin (HP/N- TiO_2). Nanoparticles of N-doped TiO_2 (N- TiO_2) are used as a matrix to prepare a dye-sensitized and visible-light active photocatalyst. The synthesized N- TiO_2 nanoparticles and the hybrid nanocomposite are then characterized by different techniques and the photocatalytic activity of the products are evaluated by the degradation rate of methyl orange (MO) as a model pollutant. Accordingly, the synergism effect of nitrogen doping and HP sensitizing is discussed.

2. Experimental

2.1. Materials

Sigma–Aldrich HP ($\geq 45\%$) was used without further purification. The tetraisopropyl-orthotitanate ($\geq 98\%$), urea ($\geq 99.5\%$), ethanol ($\geq 99.9\%$), acetyl acetone ($\geq 99.0\%$), mannitol ($\geq 99.0\%$) and methyl orange (C.I. 13025) were purchased from Merck and used as received without any further purification. Fresh deionized water was prepared from a deionizer apparatus (Hastaran Co.) and used in the preparation of solutions.

2.2. N- TiO_2 and HP/N- TiO_2 preparation

The nitrogen-doped titania, N- TiO_2 , product were prepared by the sol–gel method. For this aim, tetraisopropyl-orthotitanate (2.5 mL) was slowly added to a mixture of anhydrous ethanol (20 mL) and acetyl acetone (2.5 mL) with stirring at room temperature. Acetyl acetone was used as chelating agent to prevent precipitation of the tetraisopropyl-orthotitanate. After stirring for at least 60 min, the clear and yellow solution was obtained. We then added 3.0 mL deionized water and stirred the mixture for 30 min. A few drop of concentrated HCl solution was then added to the sol to adjust the pH at about 1.7. At the next step, urea (4.0 g) was dissolved in ethanol and then added to the above solution. The mixture was stirred for 180 min at room temperature. The final solution was left overnight to form a wet gel. The wet gel was dried at 60°C and the resultant precipitate was ground in agate mortar. Finally

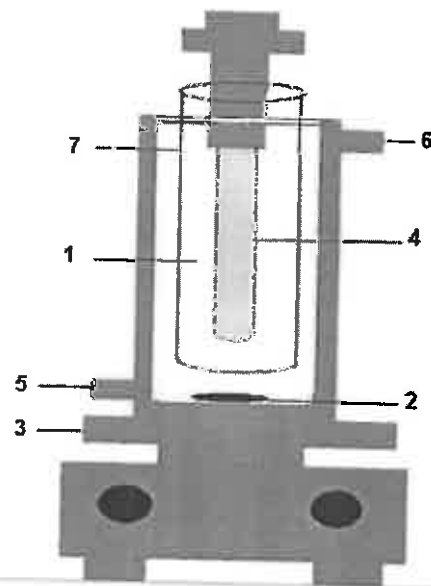


Fig. 1. Scheme of the used photoreactor; (1) dye solution; (2) magnetic stir bar; (3) magnetic stirrer, (4) visible lamp; (5) cooling water in; (6) cooling water out; (7) quartz tube.

the precursor was calcined at 550°C for 1 h. The bare TiO_2 was also prepared using a similar method unless urea addition.

The main product, HP/N- TiO_2 nanocomposite, was prepared in the way that the synthesized N- TiO_2 (1.0 g) was added into 3.0×10^{-3} M of HP solution in ethanol and the suspension was sonicated for 30 min. The mixture was stirred for 48 h at room temperature to obtain the absorption/desorption equilibrium. Finally, the solid was separated by centrifugation, washed several times with ethanol in order to remove the unloaded HP molecules and dried at room temperature. For the aim of activity comparison, HP/ TiO_2 nanocomposite was also prepared by following the same procedure. The amount of adsorbed HP was estimated by measuring the concentration of the dyes desorbed from the N- TiO_2 surface which was attained by immersing 25 mg of the HP/N- TiO_2 samples into 5 mL of NaOH solution (0.1 M) [29,30]. The absorbance of the resulting solution was measured at HP maximum wavelength of 397 nm using a UV–vis spectrophotometer (Jasco-V630) and compared with reference solutions (HP concentrations of: 0.003, 0.006, 0.009 and 0.012 mM in 0.1 M NaOH solutions).

2.3. Products characterization and photocatalytic activity

The prepared xerogels were thermally analyzed in air by a PerkinElmer Pyris Diamond apparatus at a scanning rate of $5^\circ\text{C}/\text{min}$. All samples were analyzed by a Structures-APD 2000 X-Ray Diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm) radiation in the 2θ range of 10 – 80° . The crystalline size of TiO_2 was determined according to the Scherrer equation using the full-width at half maximum (FWHM) of peak broadening. The FT-IR spectra were recorded on a PerkinElmer 65 spectrophotometer. Specific surface area of the sample was measured by BET method on Phschina 1020 at -196.15°C nitrogen adsorption–desorption mode. The UV–vis spectra of TiO_2 samples in the 200–1100 nm were recorded. The morphology of hybrid nanocomposite was determined using Zeiss-Sigma field emission scanning electron microscopy.

Photodegradation of MO in the presence of photocatalyst products was examined in a Pyrex reactor with a magnetic stirring bar and water circulating jacket (Fig. 1). The visible light source

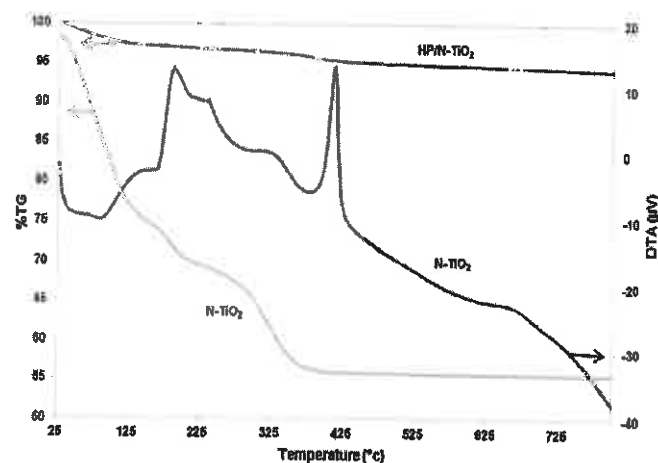


Fig. 2. TGA curves of the N-TiO₂ dry gel and HP/N-TiO₂ nanocomposite, and DTA curve of the N-TiO₂ dry gel.

was an Osram HCL-T 150 W metal halide lamp [31] (light intensity specification presented in Fig. S1), placed centrally in the reactor. The HP/N-TiO₂ nanocomposite (0.3 g) was added to 300 mL of MO solution (5.0 mg/L). In order to reach the adsorption-desorption equilibrium, the suspension was magnetically stirred in dark for 1 h, and the lamp was then switched on. The suspension was sampled at regular time intervals and rigorously centrifuged for 10 min to separate suspended nanoparticles and the concentration of MO was immediately analyzed. For comparison, the MO degradation experiment was conducted under the same conditions with each of N-TiO₂, HP/TiO₂ and bare TiO₂ nanoparticles as photocatalysts. The role of HO[•] radicals on the degradation of MO was determined by adding mannitol (0.1 M) as HO[•] scavenger.

2.4. Analytical method

The absorption spectrum of methyl orange shows a peak at 464 nm. The change of absorbance at this maximum wavelength indicates the MO degradation. The UV absorbance of the samples was measured by means of a UV-vis spectrophotometer (UV, Jasco-V630) and using the appropriate calibration curve (Fig. S2). The degradation efficiency was then calculated from $[(C_0 - C_t)/C_0] \times 100$, where C_0 and C_t denote the appropriate MO concentration at initial and any reaction time, respectively.

3. Results and discussion

3.1. Surface and structure characteristics of the samples

TG-DTA curve of the dried gel of N-doped TiO₂ nanoparticles and TGA diagram of HP/N-TiO₂ nanocomposite are shown in Fig. 2. The TG curve of N-TiO₂ dry gel includes mainly two steps. The initial weight loss (~25%) appears at the temperature range from room temperature to 150 °C. This is attributed to the evaporation of physically adsorbed water and alcohol in the xerogel. The second weight loss (~20%) between 150 and 350 °C corresponds to the combustion of organic compounds like acetyl acetone. In addition, the DTA curve reveals exothermic peaks at 425 and 700 °C. These can be attributed to the anatase phase formation and anatase to rutile phase transformation, respectively. Several endothermic and exothermic peaks are observed before 425 °C, which means that the calcining process of the composite gel includes a series of dehydration, decomposition and combustion/oxidation reactions [32]. For the HP/N-TiO₂ nanocomposite the TGA diagram shows that the loss of weight follows two steps. The first step (~3.5%) occurs from 25

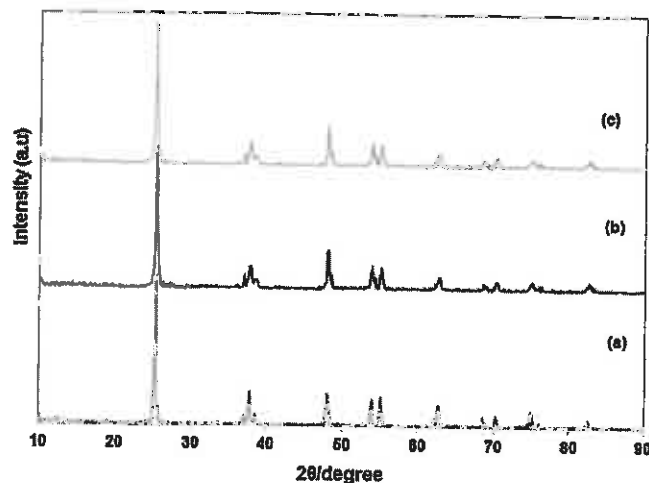


Fig. 3. XRD patterns of bare TiO₂ (a), N-TiO₂ nanoparticles (b) and HP/N-TiO₂ nanocomposite (c).

Table 1
Crystallite sizes and E_g values of the synthesized products.

Product	Size (nm)	E_g (eV)
bare TiO ₂	40.4	3.26
N-TiO ₂	29.7	2.91
HP/N-TiO ₂	29.8	2.53

to 125 °C which could be attributed to the evaporation of physically absorbed water and alcohol molecules. During the second loss (~2.5%), within the range of 125–450 °C, organic matters such as HP are combusted.

XRD analysis was carried out to investigate the crystal identity of TiO₂ samples and the effect of nitrogen and HP on the crystal structure of TiO₂. The XRD patterns of bare TiO₂, N-TiO₂ nanoparticles and HP/N-TiO₂ nanocomposite samples are shown in Fig. 3. XRD patterns of all samples demonstrate the anatase phase as the sole crystalline phase. It can be seen that the diffraction peaks of anatase phase widen and their intensity is weakened with N doping, showing the lower crystallinity and smaller size nanoparticles. No new diffraction peaks are observed in the N containing phase. The close ionic radius of N³⁻ (0.171 nm) and O²⁻ (0.144 nm) leads to the substitution of oxygen by nitrogen [33]. Using Debye-Scherrer's formula, the size of the particles was calculated from the [1 0 1] diffraction peak as [34]:

$$d = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where d is the particle size, λ is the X-ray wavelength corresponding to Cu K α radiation (0.15406 nm), β is the full width at half maximum (FWHM) of the XRD peak and θ is the diffraction angle. The crystallite sizes are listed in Table 1. The obtained size of N-TiO₂ sample is smaller than that of bare TiO₂. Peaks of the HP/N-TiO₂ nanocomposite are similar to N-TiO₂ nanoparticles. The diffraction peaks of HP were not detected in the hybrid nanocomposite which could be assigned to its complete dispersion into TiO₂ nanoparticles and low loading quantity. The peak position and peak width of HP/N-TiO₂ is same as that of N-TiO₂, indicating that the HP adsorbed on the surface of N-TiO₂ has no influence on the crystal structure and particle size of the N-TiO₂ catalyst [13,17,35].

The FT-IR spectra of pure HP, TiO₂, N-TiO₂ and HP/N-TiO₂ samples are shown in Fig. 4. The broad band at low wavenumber range from 400 to 800 cm⁻¹ can be ascribed to the strong stretching vibrations of Ti–O bond. Meanwhile, the intensity of IR band related to Ti–O–Ti vibration mode in pure TiO₂ sample is increased com-

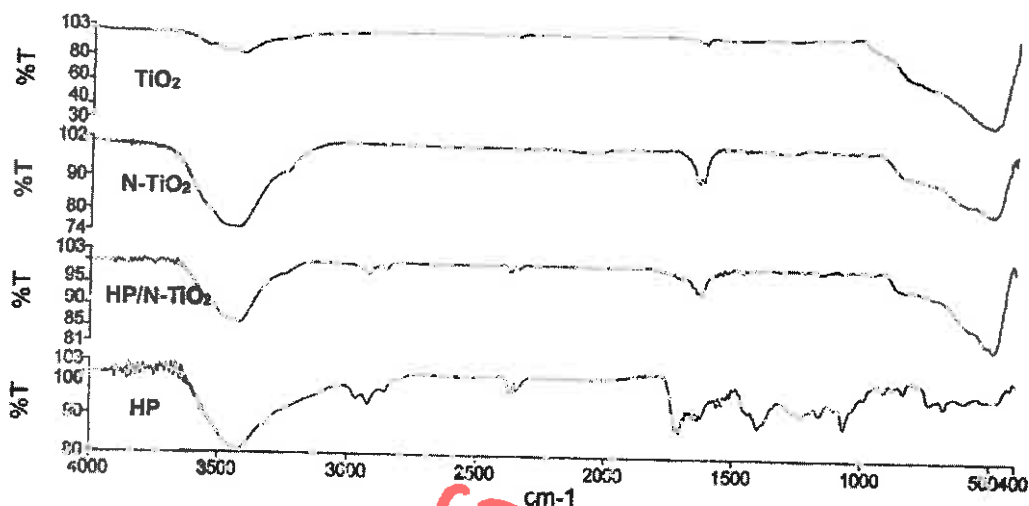


Fig. 4. FT-IR spectra of TiO_2 , N-TiO_2 and HP/N-TiO_2 nanoparticles and HP.

pared with N-TiO_2 , indicating that the corresponding anatase TiO_2 crystallinity is decreased [36] as nitrogen is doped on TiO_2 , in accordance with the XRD analysis. Additionally, two main peaks located at 3415 and 1620 cm^{-1} can be assigned to the stretching and bending vibration of hydroxyl group on the catalyst surface and water absorbed on the surface [37]. It is well known that hydroxyl groups play an important role in photocatalytic reaction. Comparing the obtained spectra, it is revealed that the intensity of the two absorption bands in the N-TiO_2 sample assigned to the hydroxyl groups is stronger than that in bare TiO_2 , indicating that doping with nitrogen favors the increase of hydroxyl groups, which was considered beneficial for the photocatalytic process [36].

After immobilization of HP on N-TiO_2 , the basic characteristic peaks for TiO_2 is hardly changed. The stretching vibrations of C–C, C–H bonds can also be observed in the supported catalyst, indicating the presence of HP on the surface of N-TiO_2 . Further, the spectra show that the peaks corresponding to the stretching vibrations of hydroxyl groups are broader and stronger in N-TiO_2 than that of supported catalysts, due to the decrease of hydroxyl groups after HP immobilization [38]. The dye used in this study, HP, contains two carboxylic groups, which possesses strong binding ability to the surface of N-TiO_2 through the $\text{O}=\text{C}-\text{O}-\text{Ti}$ bonds. For the pure dye, stretching frequencies of the carboxylic group are located at 1710 and 1440 cm^{-1} for the antisymmetric and symmetric stretching vibrations, respectively. After coordinating to N-TiO_2 surface, the stretching frequencies of the carboxylic groups are located at 1660 and 1452 cm^{-1} for the antisymmetric and symmetric stretching vibrations, respectively, providing clear evidence for deprotonation of the carboxylic group upon addition of N-TiO_2 nanoparticles. The frequency difference between the antisymmetric and symmetric stretching vibration ($\Delta = \nu_{\text{asym}} - \nu_{\text{sym}}$) is useful in identifying the binding mode of the carboxylate ligand [39]. Therefore, the Δ value estimated for HP loaded on the N-TiO_2 is found to be 208 cm^{-1} ($1660 - 1452 = 208\text{ cm}^{-1}$), which is a smaller value than that of the pure HP (270 cm^{-1}) and suggests that the binding mode of HP on N-TiO_2 is predominantly bidentate (Fig. 5).

The surface area of the N-TiO_2 and TiO_2 nanoparticles, based on BET measurements, were 24.46 and $18.32\text{ m}^2/\text{g}$, respectively. The incorporation of nitrogen ionic increases the extent of the surface area [35,40]. These results are consistent with the results of XRD analyses. The amount of HP adsorbed onto N-TiO_2 and TiO_2 powders was found to be 21.29 and $13.49\text{ }\mu\text{mol/g}$, respectively (see Section 3.2). The adsorption amount of HP on N-TiO_2 is higher than

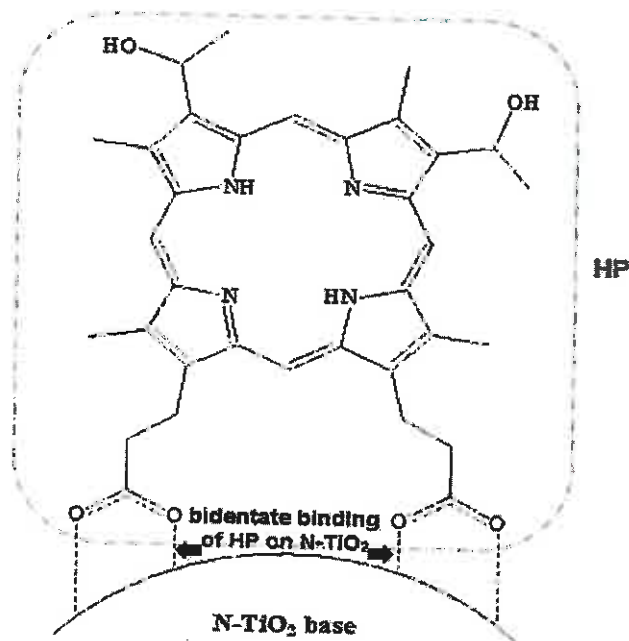


Fig. 5. Schematic illustration of bidentate binding of HP on N-TiO_2 .

that of TiO_2 . When particle diameter decreases, the quantity of TiO_2 increases per unit mass, i.e. dye loaded sites should increase [41].

The effect of N-doping and HP loading on the band structure and band gap energy is shown by absorbance spectra (Fig. 6). The visible absorption spectra illustrate that the N-doped TiO_2 is a photocatalyst with the capability of photocatalysis under visible light irradiation. Furthermore, the prepared N-TiO_2 sample has absorption band at visible light region and that the band gap energy of N-doped TiO_2 was lower than that of anatase TiO_2 . The band gap energy of the samples were determined by the following equation [42]:

$$E_g = \frac{1239.8}{\lambda} \quad (2)$$

where E_g is the band gap (eV) and λ (nm) is the wavelength of the absorption edge in the spectrum. Compared with bare TiO_2 , the band gap was changed from 3.26 to 2.91 eV . In a previous study it was showed that the reduction of the width of band gap of TiO_2 is attributed to the inclusion of nitrogen and the presence of oxy-

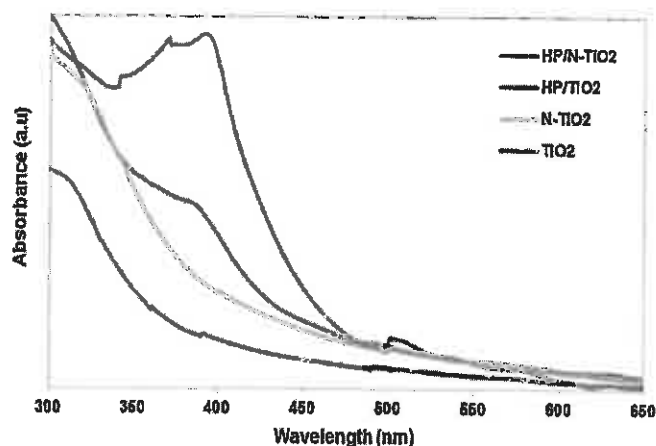


Fig. 6. UV-vis absorption spectra of different samples.

gen defects in the structure [12]. It could be deduced that mix of the O 2p states and substituted N 2p contributes in the band gap narrowing. This narrower bandgap will facilitate the transfer of electron from valance band to conduction band in the doped oxide semiconductor under visible light illumination, which can result in higher photocatalytic activities [13,43]. Thus it can be expected that the N-TiO₂ photocatalyst would demonstrate better photocatalytic activity than pure TiO₂. Obviously, there is no absorption above 400 nm for TiO₂, while the HP/TiO₂ and HP/N-TiO₂ nanocomposites exhibit the characteristic peaks of HP, indicating that HP successfully is loaded onto the TiO₂ surface while the porphyrin framework has been safely maintained. These characteristic bands were attributed to HP's Soret band and Q-band absorption [41]. Val-

ues of the band gap energies of products (E_g) have been reported in Table 1, where a red shift in the visible region from 3.26 to 2.53 eV for the bare TiO₂ and HP/N-TiO₂ photocatalysts respectively, can be seen. HP makes TiO₂ and N-TiO₂ to have a strong absorption in the region of 350–500 nm. The absorption intensity of HP/N-TiO₂ nanocomposite is much higher than that of HP/TiO₂ in the region of 350–500 nm which confirms the higher dye loading.

In order to determine the complex formation between the anchoring group of HP and N-TiO₂, we have conducted studies using UV-vis spectroscopy that is shown in Fig. S3. The HP in ethanol solution exhibits a strong Soret absorption at 397 nm together with weak Q bands between 500 and 700 nm [44]. It was therefore found that the absorption bands of the HP coupled N-TiO₂ are all red shifted relative to those of the HP in ethanol solution. The red shift of the Soret band is reasonable to conclude that HP/N-TiO₂ nanocomposite is formed by the covalent binding of N-TiO₂ and anchoring groups of HP rather than only physical adsorption [45]. Thus the change in the absorption spectra again confirms the formation of the HP/N-TiO₂ complex. The UV-vis absorption spectrum of the HP/N-TiO₂ nanocomposite was also obtained after 1 month in the dark. The UV spectrum of the aged sample was kept unchanged compared to the fresh sample, indicating that HP/N-TiO₂ was stable.

Scanning electron micrographs were used to show the morphological situation of the N-TiO₂ and HP/N-TiO₂ powders. As shown in Fig. 7(a), the N-TiO₂ has a lumpy structure, and its surface is smooth. After being treated with HP solutions, shown by Fig. 7(c), N-TiO₂ loads porphyrin and the surface contains irregular particles and becomes rough. The micrograph of N-TiO₂ with a roughly 37.9 nm diameter can also be seen in Fig. 7(b) indicating almost spherical shapes. When HP is loaded on the surface of N-TiO₂, aggregates could be observed clearly from the micrographs of HP/N-TiO₂, as

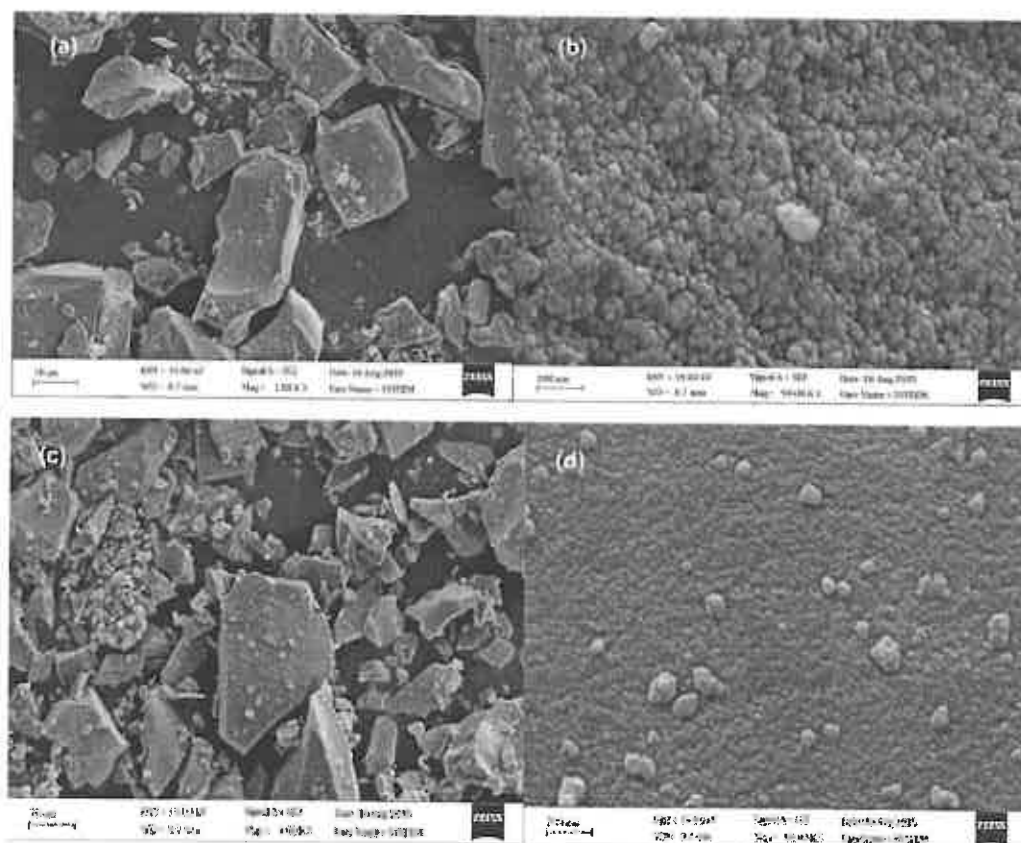


Fig. 7. SEM micrographs of N-TiO₂ (a,b) and HP/N-TiO₂ (c,d) products with different magnifications.

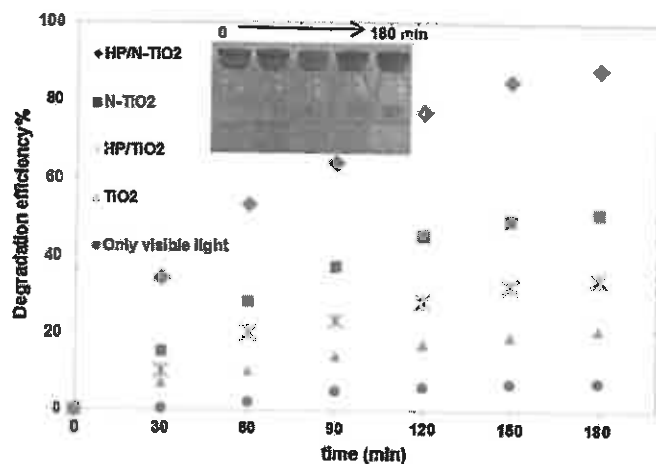


Fig. 8. Degradation efficiency vs. irradiation time of MO with different photocatalysts under visible light irradiation, $[\text{TiO}_2] = [\text{N-TiO}_2] = [\text{HP/TiO}_2] = [\text{HP/N-TiO}_2] = 1.0 \text{ g/L}$; MO initial concentration = 5 mg/L ; (inset is the image of the changes in the color of MO under visible-light illumination).

shown in Fig. 7(d). This indicates the strong adsorption occurred between HP and the TiO_2 support. As well, after HP impregnation, the micrograph of the HP/N- TiO_2 is blurred and the visualization of the N- TiO_2 structure is not clear. This confirms the presence of HP on the surface of N- TiO_2 .

3.2. Photocatalytic activity of products

The photocatalytic activity of the samples was evaluated by measuring the degradation of the organic dye MO under visible light irradiation. Fig. 8 shows the degradation efficiency with reaction time without any catalyst as well as in the presence of bare TiO_2 , N- TiO_2 and HP/N- TiO_2 samples. The direct visible light illumination without any catalyst can lead to only about 7.0% degradation within 180 min, whereas bare TiO_2 nanoparticles exhibited 21.2% degradation of MO under the same conditions. This can be accounted presumably to the self-sensitization capability of MO molecules [46]. Using N- TiO_2 , however, can lead the degradation to enhance to about 51.4% degradation, and use of HP/ TiO_2 gave an efficiency of 33.1%. The improvement of the catalytic activities through N-doping is due to the narrowed band gap of TiO_2 , as was mentioned in the previous section. After sensitizing N- TiO_2 by HP, much higher photoactivity was obtained so that degradation efficiency reached to 88.5%. It can be calculated, therefore, that the photocatalytic activity, after sensitizing of bare TiO_2 and N- TiO_2 samples, enhances to about 1.7 times. Interestingly, the photocatalytic activity increment of HP/N- TiO_2 compared with bare TiO_2 is more than the sum of increments coming from dye sensitization of just TiO_2 and N- TiO_2 . This result indicates a synergism effect between HP sensitization and nitrogen doping.

To investigate the role of MO initial concentration, different amounts of this dye were utilized under similar operating conditions. Results (Fig. S4) show a decreasing trend of degradation with initial concentration which is expected due to limited photocatalyst surface area and the light emission in contact with concentrated solutions.

The rate of the heterogeneous photocatalytic degradation of MO (5 mg/L initial concentration) has been described with the Langmuir–Hinshelwood kinetic model which can be expressed as [47]:

$$r = -\frac{dC}{dt} = \frac{kK_{ad}C}{1 + K_{ad}C} \quad (3)$$

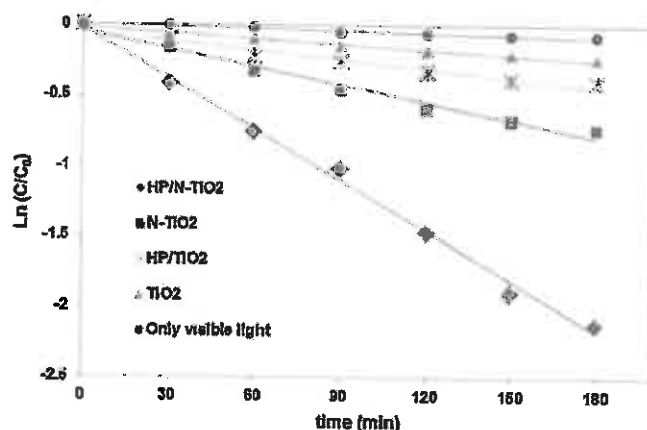


Fig. 9. The kinetics of MO photocatalytic degradation with different photocatalysts under visible light irradiation, $[\text{TiO}_2] = [\text{N-TiO}_2] = [\text{HP/TiO}_2] = [\text{HP/N-TiO}_2] = 1.0 \text{ g/L}$; MO initial concentration = 5 mg/L .

Table 2
Kinetic parameters for the photocatalytic degradation of MO under visible light.

Case	No catalyst	Bare TiO_2	N- TiO_2	HP/ TiO_2	HP/N- TiO_2
$k_{app} \text{ (min}^{-1}\text{)}$	0.0005	0.0013	0.0042	0.001	0.012
$t_{1/2} \text{ (min)}$	1386	533.2	165	693.1	57.8

where r represents the initial rate of photooxidation, C is the MO concentration at any time t , k is the reaction rate constant, and K_{ad} is the adsorption coefficient of the MO molecules on photocatalyst. At the low concentrations of MO ($K_{ad}C \ll 1$) which is the case in this work, Equation (3) can be simplified to an apparent first order equation:

$$\ln \frac{C}{C_0} = -kK_{ad}C = -k_{app}t \quad (4)$$

where $k_{app} = kK_{ad}$ is the apparent rate constant and C_0 is the initial concentration of MO. In order to evaluate qualitatively the rate of photodegradation of MO under visible light illumination, the linear relationship of the natural logarithm of the ratio between the initial concentration of MO and its concentration at different times ($\ln(C/C_0)$) versus the corresponding irradiation time is presented in Fig. 9. The results indicate that the photocatalytic degradation of MO can be described by the apparent first order kinetic model. Kinetic parameters for the photocatalytic degradation of MO are listed in Table 2.

Previous studies indicate that hydroxyl radical, $\text{HO}^\bullet$, was the major oxidant for photocatalytic degradation in wastewater treatment [20]. To determine the contribution of $\text{HO}^\bullet$ radical on degradation, mannitol scavenger (0.1 M) was added to HP/N- TiO_2 aqueous dispersion. In comparison with the main reaction (no scavenger), the MO degradation decreased to about 58% (Fig. S5) which is due to hydroxyl radical scavenging by mannitol. These results indicate that the hydroxyl radical has a significant contribution of about 42% while the peroxy radical ($\text{O}_2^{\bullet-}$) and the reactive holes provide the remaining activity.

The photocatalytic mechanism of N- TiO_2 sensitized by HP can be deduced based on above discussions and is shown schematically in Fig. 10. When the visible light irradiates on the surface of HP/N- TiO_2 nanocomposite, the electrons can be produced via two different paths. In one path, nitrogen doping can modify the band structure of TiO_2 by creating the intra-band-gap states close to the valence band edges, and the flat band potential finds a level higher than that of the conduction band of pure TiO_2 . Thus, when the visible light irradiates on the surface of the N- TiO_2 , the electrons can be excited easier from the intra-band-gap states to flat band [13].

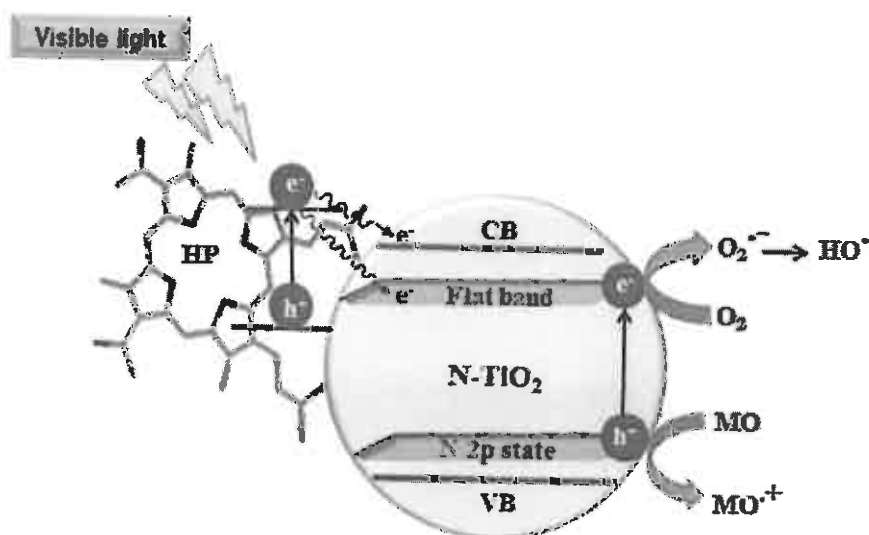


Fig. 10. Schematic illustration of the proposed mechanism for N-TiO₂ sensitized by HP in photocatalytic degradation.

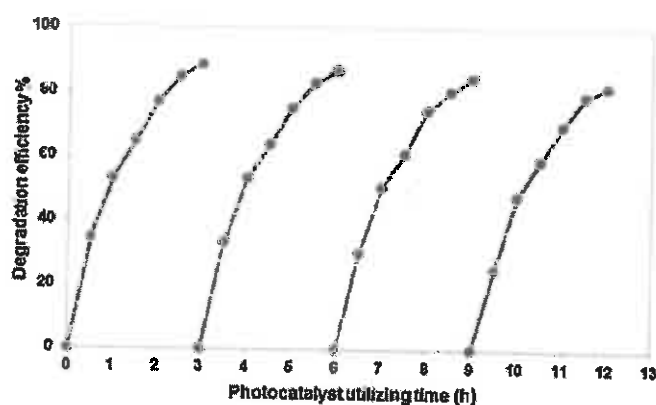


Fig. 11. Four consecutive cycles of photocatalytic degradation of MO; [HP/N-TiO₂] = 1.0 g/L; MO initial concentration = 5 mg/L.

On the other path, the HP on the surface of the N-TiO₂ nanoparticles generates photo-induced electrons by absorption of visible light. Then the photo-induced electrons transfer to the conduction band or flat band of N-TiO₂. Meanwhile HP cationic form (HP⁺) gets the electrons from the solution to reproduce HP. The reactive electrons present on the conduction band and flat band of N-TiO₂ can reduce adsorbed O₂ molecules on the surface of TiO₂ to peroxy radical (O₂^{•−}), which in-turn become highly oxidative hydroxyl radical (HO[•]) through a series of reactions, resulting in the oxidation of MO, as the final step [48]. Meanwhile, the reactive holes can oxidize MO to its radical cation either directly or through a primarily formed HO[•] produced by the oxidation of water. The synergistic effect of the HP sensitization and nitrogen doping make HP/N-TiO₂ catalyst to exhibit accelerated photoexcited electron transfer and therefore so much degradation.

3.3. Catalyst stability evaluation

In order to investigate the stability, the repeating use of the HP/N-TiO₂ nanocomposite for MO degradation was investigated. At the end of each experiment, the solution residue from the photocatalytic degradation was filtered and the HP/N-TiO₂ sample was washed and dried. The dried catalyst sample was used again for the degradation of MO under identical experimental conditions. The results show a very mild decrease (Fig. 11), confirmed that HP/N-

TiO₂ catalyst can be recycled at least four times without significant loss of activity. At the first time of HP/N-TiO₂ usage, 88.5% degradation of MO was achieved and after four cycles, the degradation efficiency retained as high as 82.1%. In addition, in UV-vis spectra (Fig. S6), it is clear that the characteristic peak of HP remains the same after four times repeating usage of the photocatalyst and that the bond between N-TiO₂ and HP is still strong and is not separated by dissolution. So, the HP/N-TiO₂ is an efficient and stable photocatalyst, merit for the degradation of organic pollutants in water under visible irradiation.

4. Conclusions

In summary, titania and nitrogen-doped titania (N-TiO₂) nanoparticles were sensitized by HP for improving the visible-light response. The new hybrid nanocomposite was methodically characterized with the aid of standard optical and microscopic techniques. Accordingly, UV-vis absorbance analysis of the prepared nanocomposite indicated that HP in hybrid nanocomposite extends the absorption of N-TiO₂ into the visible region such that visible light could be harnessed. FT-IR analysis also indicated successful binding of the dye to the N-TiO₂ surface. Due to the presence of carboxyl groups, HP can be chemisorbed on the surface of N-TiO₂ nanoparticles through the O=C–O–Ti bonds. Examining the photocatalytic activity of the hybrid nanocomposite on degradation of methyl orange under visible light showed superior degradation over pure N-TiO₂ and TiO₂ (about 4.2 and 1.7 times enhancement, respectively, compared with bare TiO₂). This high visible light activity of HP/N-TiO₂ can be attributed to the synergistic effect of titania nitrogen doping and sensitization with HP.

Acknowledgement

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molcata.2015.12.027>.

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