GERMANY/HONG KONG JOINT RESEARCH SCHEME
THE PROJECT REPORT
(for Project Completion)

Project Number: G_HK011/11

Title

Atomistic simulations of nitrogen oxides adsorption on metal oxides nanoparticles for photocatalysis

Particulars

	Hong Kong team	German team
Name of Project Co-ordinator (with title)	Prof. Rui-qin Zhang	Prof. Thomas Frauenheim
Name of Co-Investigator (if any)		Dr. Andreia Luisa da Rosa
Institution or Institutional affiliation	√ CityU; ☐ CUHK; ☐ HKBU; ☐ HKIEd; ☐ HKU; ☐ HKUST; ☐ LU; ☐ PolyU	√ University of Bremen; ☐ Others: _____
Other project team members (if any)	Kun-peng Dou	Andreia Luisa da Rosa, Svea Sauer, Jianping Xiao

Funding Period

	1st year	2nd year (if applicable)
Start Date	01-Jan-2012	01-Jan-2013
Completion Date	31-Dec-2012	31-Dec-2013

Expenditure of Hong Kong Project Co-ordinator (HK$)

1st year		2nd year (if applicable)	
Budget allocated	Unspent balance	Budget allocated	Unspent balance
15,200	15,200	15,200	0

Objective(s) as per original application

1. Employ SCC-DFTB calculations to investigate TiO_2 nanoparticles of several shapes and sizes (with rutile and anatase structures).

2 Perform SCC-DFTB calculations in order to find the optimized configurations and binding energies for the adsorption of NO and NO_2 on the nanoparticles. For this purpose, various orientations of the molecules must be tried as well as different coverages and different binding sites. Stoichiometric and defective nanoparticle facets will be taken into account.

3 Compute the optical absorption spectra for stable systems based on the TD-DFTB calculations. We will perform excited state dynamics of the TiO2 surface to understand the photocatalytic oxidation dynamics of the nitrogen oxides on the TiO2 surfaces. Explore the possible extension to other metal oxides such as ZnO and $K_2Nb_4O_{11}$.

Exchange activities taken in the whole project duration

Name of Hong Kong traveller	Dates of visit	Address of visiting institution	Purpose of visit
Rui-qin Zhang	From 4 July 2013 to 13 July 2013	University of Bremen	Discussion of results, preparation of manuscripts

Name of German traveller	Dates of visit	Address of visiting institution	Purpose of visit

Andreia Luisa da Rosa Prof. Thomas Frauenheim Jianping Xiao Prof. Thomas Frauenheim	Dec. 2012 Dec. 2012 Dec. 2012 Dec. 2013	City University of Hong Kong	Discussion of electronic structure results, set up of TDDFT optical properties calculations, preparation of manuscripts

Details of Report [Please attach relevant document(s)]

i) Outline of proposed research and results obtained

In the proposed research, first we investigate TiO_2 nanoparticles of several shapes and sizes (with rutile and anatase structures). Then we optimize the configurations and obtain the binding energies for the adsorption of various molecues on the surfaces of the optimized nanoparticles. Various orientations of the molecules are tried as well as different coverages and different binding sites. Stoichiometric and defective surfaces are taken into account. MD simulations are performed to test the stability of the calculated structures and study finite temperature effects. We then perform excited state dynamics of the TiO_2 surface to understand the photocatalytic oxidation of the nitrogen oxides on these surfaces. Finally we summarize the results, write the corresponding publications, and discuss on future collaborations.

During the project, we found that the $(TiO_2)_n$ clusters have a strong ability to adsorb water molecules and the dissociative adsorption of water molecules on the surface of $(TiO_2)_n$ clusters with a three step process is irreversible, size-dependent and energetically more favorable than the same on the surfaces of titanium oxide. Charged $(TiO_2)_n$ cluster also have strong ability in H_2O molecule splitting similar as neutral ones. The efficiency of water molecules dissociating on $(TiO_2)_n$ cluster surface varies inversely with the cluster size due to the steric effect.

In an extension of our research to ZnO surfaces, we found that under O-rich conditions, the formation of active oxygen vacancies on various ZnO surfaces is unfavorable. However, addition of Cu dopants can significantly improve the reducibility of the ZnO nonpolar and polar surfaces, to an extent that ZnO(0001)-O polar surface can be fully reduced. The formed oxygen vacancies in turn enhanced the charging of Cu active sites on the highly dispersed metallic monolayers containing Cu and Zn. This is believed to be a factor contributing to the synergetic effects of Cu/ZnO catalysts. Irreversible reconstruction of the active metallic monolayers would take place upon removal from the reactive environment and exposure to ultrahigh vacuum condition, resulting in less active Cu overlayers. Therefore, experiments performed directly under UHV may underestimate the activity of the actual catalysts under reactive environment.

ii) Significance of research results

Our results indicate a higher efficiency of small clusters of titanium oxide in dissociating water molecules than its low index surfaces of bulk terminated and thus have significant impact on the development of size dependent nanocatalysis.

The extension of our research to ZnO surfaces revealed the self-adaptive behavior of the industrial Cu/ZnO active sites under different atmospheres. The most stable Cu(111) and reactive Cu(211) surfaces decorated by Zn atoms, commonly observed under UHV conditions do not necessarily represent the actual active surface in the industrial process.

iii) Research output

Hongbo Du, Abir De Sarkar, Haisheng Li, Qiang Sun, Yu Jia*, Rui-Qin Zhang*, "Size dependent catalytic effect of TiO2 clusters in water dissociation", **Journal of Molecular Catalysis A: Chemical**, 366, 163–170 (January 2013).

Jianping Xiao, Andreia L. Rosa, Ruiqin Zhang, Wey Yang Teoh, Thomas Frauenheim, "Structural Evolution of Cu/ZnO Active Sites: From Reactive Environment to Ultrahigh Vacuum", **ChemCatChem**, in press.

iv) Potential for or impact on further research collaboration

The research has brought the two groups to an even closer relationship for wider researches. The knowledge sharing of methodology is particularly helpful for our future research. The project appears to be a good foundation to form group research proposals such as Corporative Research Fund in Hong Kong.

Signatures and Dates

Hong Kong Project Co-ordinator
Date: 8 June 2014

Hong Kong Institution's Representative
Head of Department
Date:
- 9 JUN 2014