中国科学院大连化学物理研究所
优秀博士后支持计划申请表

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研　究　组：05T7 组

学科专业：化学工程

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	2016 年 2 月-2017 年 12 月	里尔第一大学（Université Lille 1）	博士后
	2018 年 2 月-2018 年 10 月	悉尼大学（University of Sydney）	博士后研究员
	2018 年 6 月-2018 年 10	中国科学院大连化学物理研究所	访问学者
	2018 年 10 月-今	中国科学院大连化学物理研究所	博士后
博士学位	博士论文题目	**The photocatalytic treatment of shower water in a pilot scale reactor: Experimentation and modelling**	
	指导教师姓名	**Prof Vishnu K. Pareek**	

论文摘要	（限 **800** 字） This research looked at the feasibility of photocatalysis for the treatment of greywater. The type of greywater chosen was real shower water, which was collected at the researcher’s home for treatment in a pilot scale slurry photocatalytic reactor with diameter of 30 cm and maximum capacity of 31 L. Experiments showed that up to 57% of total organic carbon (TOC) elimination was obtained after 6 hours of treatment at the following optimum conditions: pH = 3.0, catalyst concentration = 0.07 gL-1, air flow rate = 1.8 Lmin-1 and slurry recirculation rate = 4.4 Lmin-1. The ease of operation and control of the reactor (at ambient conditions) showed that photocatalysis could be successfully transposed from bench scale to pilot scale. Due to the unavailability of the optical parameters for the catalyst used in this research (Aeroxide® P25 TiO_2), experiments were performed at typical catalyst concentrations (0.05 and 0.10 gL^{-1}) to measure the light intensity distribution within the slurry reactor. The values obtained were then replicated by computational fluid dynamics modelling (CFD) by changing the inputs for the optical parameters (absorption and scattering coefficients) until a satisfactory fit to the experimental readings were obtained. It was found that a wavelength averaged value for the scattering coefficient could be used (analogous to that of Degussa P25 TiO2) but the absorption coefficient was comparatively higher (in the UV-C region) and was wavelength dependent. As a result, the UV emission spectrum of the lamp used in this research was divided into 3 bands for which the absorption coefficients were determined. These optical parameters were of paramount importance in the radiation and species modelling inside the photocatalytic reactor. A general rate equation applicable to slurry reactors with large diameter was devised and used for the rate modelling of the pollutant degradation. The rate equation took into consideration all the reaction regimes existing in the reactor (half order, transitional order and first order) with respect to the local volumetric rate of energy absorption (LVREA). In the modelling of the pollutant degradation in the reactor, the transitional regime was ignored for simplicity. By a trial and error method, it was found that using a

value of 225 Wm-2 as the minimum incident light intensity at which half order reactions take place, a Pearson correlation coefficient of 0.88 between simulated and experimental data indicated model adequacy. Moreover, it was established that the average reaction rate was largely dependent upon first order reaction (up to 20 times higher than half order reactions) because of the square root dependency of the reaction rate with respect to the LVREA at high incident light intensities (since high electron-hole recombination lead to reduced reaction).

Finally, simulations of the photocatalytic reactor using 2 and 4 lamps at different geometrical placements instead of one powerful lamp in the middle of the reactor were implemented. It was found that within the range of catalyst concentrations investigated, multiple lamps arrangement resulted in higher average reaction rate with a maximum potential increase in reaction rate of 56% and 123% with 2 and 4 lamps respectively. The significant increase in reaction rate was attributed to a maximisation of incident radiation contours at which first order reactions took place when using multiple and less intense lamps instead of only a powerful one. The optimum lamp separation at which maximum reaction rate arose did not necessarily occur at the optimum lamp separation for which maximum LVREA occurred.

入站前期科研情况简介

1、主持或参与项目情况：

序号	项目名称	项目来源	项目金额	起止年度	角色

2、论文发表情况：（已发表或已接收发表）

序号	论文题目	期刊名	影响因子	发表年度/卷期/页码	排序
1	**From waste Coca Cola® to activated carbons with impressive capabilities for CO_2 adsorption and supercapacitors**	**Carbon**	**6.337**	**2017/116/490-499**	**1**

	2	Synthesis and applications of porous non-silica metal oxide submicrospheres	Chemical Society Reviews	38.618	2016/45(21)/ 6013-6047	1
	3	A review on photocatalysis for air treatment: From catalyst development to reactor design	Chemical Engineering Journal	6.216	2016/310/537-559	1
	4	Synthesis of $CaCO_3$@C yolk–shell particles for CO_2 adsorption.	RSC Advances	3.108	2015/5(32)/ 24872-24876	1
	5	Synthesis of micro and nano-sized calcium carbonate particles and their applications	Journal of Materials Chemistry A	8.867	2014/2/ 14270-14288	1
	6	CFD simulation of a pilot scale slurry photocatalytic reactor and design of multiple-lamp reactors	Chemical Engineering Science	2.895	2014/111/ 266-277	1
	7	Lamp emission and quartz sleeve modelling in slurry photocatalytic reactors,	Chemical Engineering Science	2.895	2014/111/34-40.	1
	8	Some aspects of photocatalytic reactor modelling using computational fluid dynamics	Chemical Engineering Science	2.895	2013/101/764-784	1
	9	Light Intensity Distribution in Multi-Lamp Photocatalytic Reactors	Chemical Engineering Science	2.895	2013/93/ 11-21	1
	10	A Review of Greywater Characteristics and Treatment Options	Water Science & Technology	1.197	2013/67/ 1403-1424	1
	11	Photocatalytic Treatment of Shower Water Using a Pilot Scale Reactor	International Journal of Photoenergy	1.547	2012/1-7	1

	12	**Advanced yolk-shell nanoparticles as nanoreactors for energy conversion**	**Chinese Journal of Catalysis**	**3.525**	**2017/38(6)/ 970-990**	**2**
	13	**Removal of dyes from aqueous solution using fly ash and red mud**	**Water Research**	**7.051**	**2015/39/129-138**	**2**
	14	**A comparative study of dye removal using fly ash treated by different methods**	**Chemosphere**	**4.427**	**2005/60/1401-1407**	**2**
	15	**Role of unburnt carbon in adsorption of dyes on fly ash**	**Journal of Chemical Technology and Biotechnology**	**2.504**	**2005/80/1204-1209**	**2**
	16	**Zeotisation of fly ash for sorption of dyes in aqueous solutions**	**Studies in Surface Science and Catalysis**		**2005/158/161-168**	**2**
	3、专利情况：					
	序号	专利名称	授权/申请	授权/申请号	起始日期	排序
	4、获奖情况：					
	序号	奖励名称	奖励等级	授奖单位	奖励年度	排序
		European Postdoctoral Fellowship AAP “Mobilité entrante 2015” du conseil regional Nord-Pas de Calais for young researchers		法国	**2015**	**1**
	博士后研究题目：**Yolk-Shell Nanoparticles for Conversion of CO_2 into Renewable Fuels: From Nano-Bioreactor to Photocatalytic Reactor Engineering**					

博士后工作的研究计划	（简述研究计划的可行性、先进性和创新性，理论和现实意义） **Main research** ***This project deals with the conversion of CO_2 into useful fuels by engineering the catalyst development at the nano and micro-scale as well as photocatalytic reactor design at the meter-scale. A nanoscale bioreactor that integrates enzymes with photocatalysts to efficiently convert CO_2 into renewable fuel will be synthesized. Following this, photocatalytic reactors at the pilot scale will be built and optimally designed by performing simulations and modeling by computational fluid dynamics (CFD).*** We will combine leading-edge nanoparticle technology with enzyme engineering in the design of a reactor that simultaneously achieves the capture and conversion of CO_2 by artificial photosynthesis. The key concept and strategy lies in the use of unique yolk shell nanoparticles (YSNs) to assemble two enzymes and a photocatalyst system into a single nanoreactor in the desired spatial organization. Specifically, the core and shell of YSNs will be separately functionalized to allow the selective immobilization of an enzyme, with the shell-enzyme for CO_2 capture and the core-enzyme for conversion of CO_2 (**Fig. 1a**). Importantly, the conversion enzyme assembled on the core is directly linked with the photocatalyst (metal core) that will be engineered to utilize light in the visible wavelength range to produce free electron/hole pairs for CO_2 reduction. This designed structure which allows the spatial arrangement of immobilized enzymes at two levels is expected to simultaneously maximize capture of CO_2 at YSNs surface and conversion of CO_2 within YSNs, thus **achieving a highly efficient nano-bioreactor for sustainable production of fuels. To: (1) understand the energetic interaction between substrate and catalyst surface, (2) estimate the electron/hole band-gap separation of the catalyst at the nano-scale and (3) calculate the mass transfer kinetics of substrate and products at the micro-scale, modeling softwares such as DFT and MATLAB will be used to help optimize the bioreactor reactor design (crystal size and phase, yolk-shell design and material choice for yolk and shell) at the small scale. Then, CFD modeling will be used to optimize several gas-phase reactor designs at the larger meter-scale by simulating the light radiation distribution, hydrodynamics and reactant conversion (due to light absorption) inside the photocatalytic reactor. Following the designs, the reactors will be built and tested at the pilot-scale for possible large-scale commercialization.** **Target** *(1) to simultaneously achieve CO_2 capture and conversion in a single nano-bioreactor.* We will tailor YSNs with controlled functionality both on the silica shell and the metal core in order to assemble enzymes together with the photocatalyst in the desired spatial arrangement. Specifically, the surface of the nanoparticle shell will be designed to immobilize the enzyme - **carbonic anhydrase** (**CA**) - that can efficiently capture CO_2 and the surface of the core nanoparticle will be functionalized for immobilization of another

enzyme - **formate dehydrogenase** (**FDH**) - that can convert CO_2 into formic acid. This design of nano-bioreactor can capture and concentrate CO_2 for its subsequent reduction within YSNs, maximizing conversion yield of the nano-reactor.

(2) *to integrate photocatalysis from solar energy with biocatalysis of CO_2 conversion.* The existing technology can achieve relatively high solar energy utilization by producing sufficient free electrons. However, most of these electrons are lost due to poor electron utilization in the CO_2 conversion step. This inefficiency is due, in part, to poor coupling between photocatalyst and biocatalyst and photocatalyst type [1]. We will control the density and orientation of enzyme FDH on the metal photocatalyst surface to enhance electron utilization and will optimize the photocatalyst (material type such as doped-TiO_2 [2,3], CdS [4], crystal phase, size and orientation).

(3) *to discover new fundamental knowledge in understanding the structure-function relationship of the nano-bioreactor.* We will systematically study the effects of particle size, shape, porous structure and surface functionality of the YSNs on the biocatalytic performance of assembled enzymes and light utilization efficiency of the photocatalyst. This structure-function relationship will be used to guide design of the next generation of nano-bioreactors to enhance efficiency of CO_2 conversion.

(4) *to determine the optical parameters of the catalyst.* Since the photocatalyst will be new, its optical parameters such as adsorption and scattering coefficients will need to be determined experimentally. The photocatalyst will be designed to be able to absorb maximum light within the visible wavelength band range, so as to be viable for solar application. These parameters are essential for the further design and modeling of photocatalytic reactors.

(5) *to determine the kinetics of the reaction.* We will carry out in-situ spectroscopy techniques to investigate the reaction mechanisms and steps involved to devise a reaction rate equation. The intrinsic reaction kinetics for the CO_2 conversion process (including the reaction rate constants) will then be determined on the bench scale so as to be used for the optimization of larger scale photocatalytic reactors [5].

(6) *to design reactor from the nano-scale to micro-scale and then meter-scale.* DFT modeling will be used to understand the basics of the physico-chemical interaction between catalyst and substrate so as to optimize the design of the bioreactor at the nano-scale level (crystal size, phase and orientation). DFT will also help to estimate the band-gap energy separation due to light interaction with the catalyst, for optimizing and proper choice of material as the core of the yolk-shell bioreactor for maximum use of light radiation in the visible electromagnetic range. Further, computational softwares will be used to understand the effects of mass transfer (and its limitations) of the substrate and product molecules to and from the bioreactor. Understanding this will allow us to optimize the yolk-shell reactor in terms of pore size, void

(between core and shell) size and shell thickness. Furthermore, in-situ spectroscopy techniques will help understand the mechanism and kinetics of adsorption and desorption of substrate/product for optimizing the bioreactor in terms of core and shell material. CFD will then be used (see part 7) to optimize the photocatalytic reactor at the large scale.

(7) *to design of photocatalytic reactors.* Various reactor designs such as monolith or packed-bed reactor will be designed, engineered and fabricated. The reactors will use light from an outside source such as multiple UV-Vis lamps. CFD modeling can be used to model the hydrodynamics as well as light radiation distribution within the reactor via different lamp emission models [6]. The optical parameters and the light radiation distribution will then be used to determine the local volumetric rate of energy absorption (LVREA) of the catalyst in the proposed reactors which will be factored into the intrinsic rate equation to simulate the kinetics and reactant conversions in the reactors [7]. As such, for each reactor model proposed, the optimum reactor design in terms of light distribution, reduced mass transfer limitations and maximum conversion, can be determined for eventual engineering, building and testing.

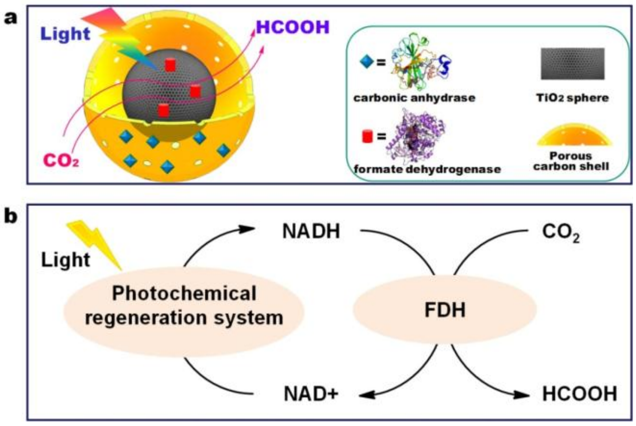

Figure 1. (a) Schematic illustration of the nano-bioreactor design in the current proposal; CO_2 is captured by carbonic anhydrase at the shell, and conversion is realized by formate dehydrogenase within the shell. (b) Reaction scheme of the reduction of CO_2catalysed by formate dehydrogenase (FDH) with cofactor NADH and mediated by the photochemical regeneration system.

Significance of project

The continued use of fossil fuels as our main source of energy leads to two major issues: (1) rapid depletion of natural resources and (2) large release of the greenhouse gas CO_2, which is a potential contributor to the effect of global warming. One possible sustainable solution is to capture and reuse the emitted CO_2 for conversion into useful fuels. In this project, we take heed of mother nature and its mechanism of photocatalysis, a process used by plants to convert CO_2 into energy in the presence of sunlight. However, the current artificial photosynthesis system is unsuitable for CO_2 conversion because the individual reaction components of the system are poorly combined. *There is a pressing need for new approaches that can integrate enzymes with photocatalysts to efficiently capture and convert CO_2*. This research will deliver a new technology combining bioengineering and nanotechnology, building on research strengths of the Design and Synthesis of Micro and Nano Reactors group, directed by Professor Jian Liu at Dalian Institute of Chemical Physics (DICP).

In this project, we will develop yolk-shell based nano-bioreactors which are simple to use and tailored for integration of enzymatic reactions with photocatalysts. The success of this research will provide a powerful and flexible platform which can efficiently assemble all the reaction components into a single nano-reactor to promptly capture CO_2, efficiently harvest light and successfully maximize enzyme conversion of CO_2 into formic acid. This, in turn, will lead to a self-sustained technology that harnesses and stores solar energy into storable fuels.

Innovation of project

The designed yolk shell structured nano-bioreactor enables the following: *i). tailoring of enzyme quantity according to enzyme activity; ii). ordered assembly of enzymes within nanometer distances to facilitate substrate channeling and direct transfer of reaction intermediates and cofactors between consecutive enzymes without equilibrating with the bulk fluid; iii). fine adjustment of pore size of the scaffold to acquire low mass transfer resistance for the intermediates/products; iv). easy recovery and recycling of immobilized enzyme.* Specifically:

1. The unique architecture and easily modulated surface properties of YSNs promise an innovative approach for the creation of a highly efficient nano-bioreactor for fuel production from CO_2. The external surfaces of YSNs are occupied by CA to maximize CO_2 capture while the internal spaces are utilized by photocatalyst and FDH to maximum conversion of CO_2. ***This novel design will concentrate CO_2 for subsequent reduction, to achieve the cooperative action of two enzymes and one catalyst within a single nanoparticle.***
2. *YSNs synthesis*: *Novel YSNs with desired chemophysical characteristics such as: large cage and controlled shell thickness, multifunctional surface groups, magnetic and photocatalyst core, selectively located functional group and enzymes both on the core and shell. This structure will be synthesized for the first time.* YSNs with a unique core@void@shell nanostructure are promising candidates as nanoreactors for cascade reactions owing to the easy functionalisation of both the core and the shell, the high density of exposed active sites endowed by the movable core, and the protection effect endowed by the shell, especially under harsh reaction conditions.
3. *Selective functionality*: Since each core in the YSNs is *isolated* by a permeable shell and has a relatively *homogeneous environment*, enzyme can be accurately located in the core or on the shell. This arrangement provides the possibility of designing and fabricating *solid nanoreactors for cascade reactions*. By

positioning different types of enzymes in separate domains we will be able to *mimic the compartmentalization of biological reactions seen in natural systems*.

4. *By integrating enzymes and nanoparticles* into the same cavity of YSN support, a specific environment is created where these species can reside and act in close proximity to one another in a cooperative fashion, thus enhancing the *confinement effect*. This designed nano-structure will ensure true cooperativity by simultaneously realizing sequential reactions of CO_2 capture and conversion and by effectively using free electrons produced from light energy.
5. The immobilization strategy and the solid shell of YSNs facilitate to promote the *long-term stability* of the key bio- and photochemical elements as well as enable *the reuse of this elaborately organized system*.
6. *In-situ spectroscopy techniques* used in this proposal will make the investigation of the *reaction mechanism* relatively straightforward and provide important experimental evidence for understanding the reaction steps involved. These fundamental works therefore can further guide the structural optimization for the yolk shell structured functional catalysts. The reaction steps will be helpful to devise the reaction kinetics for later use in the design and modeling of photocatalytic reactors.
7. *Production of fuels*: The bio-nanoreactor can reduce greenhouse gas emissions while creating a renewable fuel.
8. *Determination of the reaction kinetics*: bench scale tests will be carried out to determine the kinetics of the reaction. Furthermore, the optical parameters of the catalyst need also be determined. The kinetics and optical parameters will be essential for the design and modeling of pilot-scaled photoreactor.
9. *CFD modeling*: CFD modeling will be performed to understand the hydrodynamics and light radiation utilization efficiency of different reactor types (e.g., parallel plates, monolith, packed bed, etc.) for optimal reactor design prior to construction.
10. *Design of photocatalytic reactors*: photocatalytic reactor models of different types will be designed and built for pilot scale trials to determine the amenability of the designed system for large scale production of fuels from CO_2.

Feasibility of the project

This project is based on joint research ranging from the synthesis of yolk shell particles and photocatalysis, to enzyme design and immobilization, and biocatalytic performance of nanoporous materials. The complementary research skills of the Design and Synthesis of Micro and Nano Reactors team together with collaborations with other groups will ensure that this project is well designed with clear aims, problems and feasible methodology.

The applicant is currently working as a post-doctoral fellow at Dalian Institute of Chemical Physics (DICP), in the Micro Nano Reactor and Reaction Engineering Science group led by Professor Jian Liu. Professor Jian Liu is a world known eminent specialist in the design of YSNs and their applications [8-12]. The team, which continues to grow consists of 2 post-doctoral fellows (including myself) and 8 PhD and Masters students. The team is perfectly well equipped in terms of scientific knowledge, YSNs synthesis experience, laboratory needs and characterization equipment for the synthesis and characterization of the YSNs. My experience in catalyst synthesis as well as CFD and photocatalytic reactor modeling will be essential for this project. I will also liaise with Professor Vishnu Pareek (also a CFD expert and my PhD supervisor) from Curtin University in Perth, Australia for collaborations in terms of reactor design, engineering and building at the pilot-scale level. Collaboration with also be required with Dr He, senior lecturer in the Department of Chemical Engineering at Monash University, Australia for biomolecular design, nanotechnology and bioprocessing and Dr Haritos, Principal Research Scientist at CSIRO, Australia, for her expertise in the design of enzymes (particularly carbonic anhydrases) and functional test of enzyme-nanoparticle complexes. Professor Liu has already had previous works with the latter mentioned names, which will facilitate partnership and collaborations for this project.

Expectations

The proposed research will deliver a novel nano-scale reactor that can efficiently integrate existing reaction components into an efficient artificial photosynthesis system to harvest light and convert CO_2 into fuel. It is expected that the discovered knowledge will advance the field by integrating bioengineering with nanotechnology to enable a practical nano-reactor for this purpose. The success of this research will overcome significant barriers in biocatalysed artificial photosynthesis, particularly, its low efficiency [1]. Reactor modeling and design from nano to meter-scale using the high-efficiency catalyst will pave the way towards the eventual commercialization of this technology. This multidisciplinary research will thus have significant impacts on several major technological fields including nanotechnology, energy conversion, production of high value chemicals, molecular modeling, photocatalytic reactor modeling and reactor design and engineering. Furthermore, the project will bring important economic and environmental benefits by tackling critical energy and environment issues which are: greenhouse gas (CO_2) capture and utilization and liquid fuels generation from renewable resources.

	References [**1**]. Lee S. H. *et al.*Photobiocatalysis: Activating Redox Enzymes by Direct or Indirect Transfer of Photoinduced Electrons. *Angew. Chem. Int. Ed.* (2017). [**2**]. Ohno T. *et al.*Preparation of S-doped TiO2 photocatalysts and their photocatalytic activities under visible light. *Appl. Catal. A: Gen.*, **265**, 115-121 (2004). [**3**]. Xu A. W. *et al.* The preparation, characterization, and their photocatalytic activities of rare-earth-doped TiO_2 nanoparticles. *J. Catal.*, **207,** 151-157 (2002). [**4**]. Zhang W. *et al.*Highly efficient and noble metal-free NiS/CdS photocatalysts for H2 evolution from lactic acid sacrificial solution under visible light. *Chem. Commun.*, **46,** 7631-7633 (2010). [**5**]. Boyjoo Y. *et al.* A review on photocatalysis for air treatment: From catalyst development to reactor design. *Chem. Eng. J.*, **310,** 537-559 (2017). [**6**]. Boyjoo Y. *et al.* Lamp emission and quartz sleeve modeling in slurry photocatalytic reactors. *Chem. Eng. Sci.*, **111,** 34-40 (2014). [**7**]. Boyjoo Y. *et al.* CFD simulation of a pilot scale slurry photocatalytic reactor and design of multiple-lamp reactors. *Chem. Eng. Sci.*, **111,** 266-277 (2014). [**8**]. Liu, J. *et al*. Yolk/shell nanoparticles: new platforms for nanoreactors, drug delivery and lithium-ion batteries. *Chem. Commun*. **47**, 12578-12591 (2011). [**9**]. Liu, J., Qiao, S. Z., Hartono, S. B. & Lu, G. Q. Monodisperse yolk-shell nanoparticles with a hierarchical porous structure for delivery vehicles and nanoreactors. *Angew. Chem. Int. Ed*. **49**, 4981-4985 (2010). [**10**]. Liu, J. *et al*. Yolk-shell hybrid materials with a periodic mesoporous organosilica shell: Ideal nanoreactors for selective alcohol oxidation. *Adv. Funct. Mater*. **22**, 591-599 (2012). [**11**].Liu, J. *et al*. A facile soft-template synthesis of mesoporous polymeric and carbonaceous nanospheres. *Nature Commun*. **4**, 2798 (2013). [**12**]. Liu, J. *et al*. Extension of the Stöber method to the preparation of monodisperse resorcinol-formaldehyde resin polymer and carbon spheres. *Angew. Chem. Int*. Ed. **50**, 5947-5951 (2011).
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