FDS8 (Oct 2019)

RGC Ref. No.: UGC/FDS25/E08/20 (please insert ref. above)

RESEARCH GRANTS COUNCIL COMPETITIVE RESEARCH FUNDING SCHEMES FOR THE LOCAL SELF-FINANCING DEGREE SECTOR

FACULTY DEVELOPMENT SCHEME (FDS)

Completion Report

(for completed projects only)

Submission Deadlines:	1.	Auditor's report with unspent balance, if any: within six months of
		the approved project completion date.
	2.	Completion report: within <u>12</u> months of the approved project
		completion date.

Part A: The Project and Investigator(s)

1. Project Title

Hydrogen on demand - Development of hydrogel-based hydrogen generator using single atom strategy for flexible power devices

一種基於單原子及水凝膠的微型儲氫產氫裝置的研發

2. Investigator(s) and Academic Department(s) / Unit(s) Involved

Research Team	Name / Post	Unit / Department / Institution
Principal Investigator	Dr/TSANG Chi Wing/Assistant Professor	Faculty of Science and Technology/ Technological and Higher Education Institute of Hong Kong
Co-Investigator(s)	Prof. Dr/SHAO Minhua/Professor	Department of Chemical and Biological Engineering/Hong Kong University of Science and Technology
Co-Investigator(s)	Prof. Dr/NI Meng/Professor	Department of Building and Real Estate/Hong Kong Poly University
Co-Investigator(s)	Prof. Dr/GATES Derek/Professor	Department of Chemistry, University of British Columbia, BC, Canada
Co-Investigator(s)	Dr/LU Xiao-Ying/Assistant Professor	Faculty of Science and Technology/ Technological and Higher Education Institute of Hong Kong
Others	N/A	N/A

3. Project Duration

	Original	Revised	Date of RGC / Institution Approval (must be quoted)
Project Start Date	1 Jan 2021	N/A	11 Sept 2020
Project Completion Date	30 Jun 2023	N/A	11 Sept 2020
Duration (in month)	30 months	N/A	11 Sept 2020
Deadline for Submission of Completion Report	30 Jun 2024	N/A	11 Sept 2020

4.4 Please attach photo(s) of acknowledgement of RGC-funded facilities / equipment.



Part B: The Final Report

5. Project Objectives

5.1 Objectives as per original application

1. To maximize yield of mechanical robust hydrogel derived from lignin materials with high swelling capacity by lignin functionalization.

2. To design catalytic hydrogel with high catalytic performance for hydrogen release using single-atom embedment strategy.

3. To demonstrate the flexible hydrogen generator for continuous release of hydrogen; and to gain a fundamental understanding of the reaction between the single atom and ammonia borane for rational design of catalyst.

5.2 Revised objectives

Date of approval from the RGC:	N/A
Reasons for the change:	N/A

5.3 Realisation of the objectives (Maximum 1 page; please state how and to what extent the project objectives have been achieved; give reasons for under-achievements and outline attempts to overcome problems, if any)

Objective 1 - To maximize yield of mechanical robust hydrogel derived from lignin materials with high swelling capacity by lignin functionalization.

We have found a facile one-pot way to make mechanical robust lignin-derived hydrogel: 0.05 g of hydroxyethyl cellulose (HEC) powder and a certain amount of alkali lignin were dissolved in 0.8% borax solution to create a total mixture mass of 4.85 g. The mixture was placed in an oil bath at 90°C and stirred at 400 rpm for 10 minutes, allowing the lignin and HEC to dissolve uniformly. After removing the mixture from heat, 0.15 g of polyvinyl alcohol (PVA) was added and dispersed evenly throughout the solution using magnetic stirring. This prevented agglomeration of the PVA. The mixture was then heated again in the 90°C oil bath with magnetic stirring for 60 minutes. The final pH of the mixture cooled to room temperature, a homogeneous and stable lignin-derived hydrogel was formed. Without any lignin added, the hydrogel exhibited a storage modulus (G') and loss modulus (G") of 170 Pa and 120 Pa, respectively, with elongation rate of 16. With 1 % of lignin addition, the G' and G" are 1,000 Pa and 670 Pa, respectively with elongation rate of 35. With further addition of 2% of lignin, both the G' and G" dropped half, respectively.

Objective 2 - To design catalytic hydrogel with high catalytic performance for hydrogen release using single-atom embedment strategy.

The above hydrogel was further embedded with our cobalt single-atom doped carbon nanotube **Co/CoNx-CNTs** (See Objective 3) to prepare the lignin-derived Co catalytic hydrogel (Figure 1a)

and the freeze-dried (Figure 1b) version. The ammonia borane hydrolysis reaction demonstrated that the hydrogen can be continuously released successfully (Figure 1c).



Figure 1 a) Lignin derived catalytic hydrogel with 1% lignin; b) the freeze-dried hydrogel; c) the hydrolysis of ammonia borane with the synthesized catalytic hydrogel, condition: 40°C, 0.8 g catalytic hydrogel containing 0.03 g Co-N-CNT single atom catalyst.

Objective 3 - To demonstrate the flexible hydrogen generator for continuous release of hydrogen; and to gain a fundamental understanding of the reaction between the single atom and ammonia borane for rational design of catalyst.

We have prepared a type of single atom catalyst which can outperform the conventional nanoparticle catalyst during the continuous hydrogen release reaction from ammonia borane. (Part C(9) ref 3) Citric acid solution was used to assist the dispersion of the metal into melem- C_3N_4 and to increase the specific surface area of the prepared carbonized catalysts. The composition of the citric acid solution was formulated as 50% water, 50% ethanol (95%) and citric acid (10 g L⁻¹). $Co(acac)_2$ can be atomically dispersed in DCD-350, due to weak van der Waals forces. Nominal weight ratios of Co metals to DCD-350 (1:33.3) at 800 °C were denoted as Co/CoN_x-CNT-33-800T. DCD-350 (10 g) and Co(acac)₂ (1.3 g, 5.05 mmol) were weighed and manually ground into fine particles. Citric acid solution of (6 mL) was then added to the solid mixtures. The solid mixture was subsequently dried in an oven at 100 °C for 4 hours. Afterwards, the dried mixture was further powdered using a mortar and pestle. 17 g of ceramic marbles were then added, and the solid mixture was continuously ball milled for 1 hour in an alternate motion setting. The powder was then separated from the ceramic marbles using a filter. The powder was then placed in a tubular furnance and heated to 800 °C for 2 hours at a heating rate of 2.6 °C min⁻¹ under an Ar atmosphere (flow rate $= 150 \text{ mL min}^{-1}$), followed by natural cooling to room temperature. It was found that the highest specific hydrogen generation rate can reach up to 7833 mL_{H2} gCo⁻¹ min⁻¹ at 40 °C, which far exceeded most of the non-noble metal catalysts for ammonia borane hydrolysis to date. The durability of the catalyst was successfully maintained for 40 cycling tests and no obvious decay was observed. The current study presents an example of how nanoparticles and single-atoms can be synergistically exploited for heterogeneous catalysis applications.

5.4	Summary of	of objectives	addressed	to date
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Objectives (as per 5.1/5.2 above)	Addressed (please tick)	Percentage Achieved (please estimate)
1. To maximize yield of mechanical robust hydrogel derived from lignin materials with high swelling capacity by lignin functionalization	~	100%
2. To design catalytic	✓	100%

hydrogel with high catalytic performance for hydrogen release using single-atom embedment		
3 To demonstrate the		
flexible hydrogen generator for continuous release of hydrogen; and to gain a fundamental understanding of the reaction between the single atom and ammonia borane for rational design	*	100%

6. Research Outcome

6.1 Major findings and research outcome (*Maximum 1 page; please make reference to Part C where necessary*)

Co nanoparticles embedded in graphitic carbon layers with atomically dispersed CoNx active sites on carbon nanotubes were successfully synthesized. By modifying the carbonization temperature and changing the amount of the Co metal content, the optimal ratio of the Co nanoparticles to atomically dispersed Co can be tuned for best reactivity and stability of the hydrolysis of ammonia borane. It was found that Co/CoN_x -CNT-33-800T (nominal ratio of Co to DCD = 3 wt%) which was carbonized at 800 °C exhibited the best reactivity and stability towards hydrolysis of ammonia borane. It was proposed that the Co nanoparticles and atomically dispersed Co single atoms have synergistically activated ammonia borane and the water molecule, respectively. The highest specific hydrogen generation rate was found to be 7833 mL_{H2} gCo⁻¹ min⁻¹, which doubled the pure Co nanoparticles (NPs) analogue (Figure 2a) and far exceeded most of the non-noble metal catalysts for ammonia borane hydrolysis. At the same time, the nanoparticles embedded in several layers of graphitic carbon layers prevent the nanoparticles from aggregation, promising high durability, in which the reactivity did not show any obvious decay even after 40 runs (Figure 2b). The advantage of the reported synthetic method for incorporating both the nanoparticles and atomically dispersed metal atom was that it may allow the ratio of nanoparticles/atoms to be further fine-tuned to achieve optimum reactivity. (Part C(9) ref 1 & 2)



Figure 2 a) Comparison of reactivity with catalysts Co/CoN_x -CNT-33-800T, Co/CNT, leached Co/CoN_x -CNT-33-800T and CNT; **b**) cycling performance of Co/CoN_x -CNT-33-800T catalyst (40 mg) in water (10 mL), with addition of ammonia borane (1.30 mmol) to the system at 313 K in each cycle; **c**) proposed catalytic mechanism for the ammonia borane hydrolysis by Co/Co-N-CNT.

The mechanism using the synergy of the single atom and the NPs for AB hydrolysis is described as follows: First, ammonia borane coordinated with the Co nanoparticle through the activation of the B-H bond, while the N dopants coordinated with ammonia borane through the N-H bond. It was proposed that as the hydrolysis of ammonia proceeded, the reaction media became more alkaline, which facilitated the formation of the HO*-Co-N_x species. This species could lower the adsorption barrier of H₂O molecules onto the confined Co atoms. This explained why at the 8th cycle, the reactivity increased due to more atomically dispersed Co atoms being activated to form the HO^* -Co-N_x species. When the solution became more and more alkaline, HO^{*} dominated on the catalyst's surface thus blocking the coordination of H_2O molecules. At the 11th cycle, where fresh water was replenished to decrease the [OH]⁻ concentration, the reactivity was further increased. The fluctuation in the [OH]⁻ concentration eventually led to the fluctuation of the reaction rate. At the same time, the abundant CoN_x active site could donate electrons to the Co nanoparticles, making them more active in reacting with ammonia borane through oxidative addition. After a series of H₂O molecule insertions into the B-N bond, followed by the attack of the adsorbed H₂O molecule onto the B atoms through the SN_2 mechanism, the H atoms adsorbed on the nanoparticles underwent reductive elimination to release three equivalents of H₂. It is interesting to note that Co is predicted to show similar HER/ OER behavior to Pt/Ru/Ir/Rh/Ni (better performance for the HER/OER in the case of $Co-N_2C_2$ and much better than in the cases of $Co-C_4$ or $Co-N_4$) in acidic media. Although in our case, AB hydrolysis exclusively occurred in alkaline media, and this should be much more similar to the case of the HER in alkaline media, where the water was cleaved by the $OH^*-(Co-N_2)$ moiety of the Co-N₄ species. (Part C(8) ref 1 & 2)

The identity of the single atom was unequivocally proofed by X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) at the Co K-edge. As shown in Figure 3a, the white line intensity and the associated K-edge threshold of CoPc were significantly higher than that of Co foil, suggesting the dominant ionic nature of Co species in CoPc. Interestingly, the XANES spectra of Co/CoN_x-CNT demonstrated a similar feature as both of Co foil at low energy (~7710 eV) and CoPc at ~7725 eV, suggesting the presence of both metallic and ionic phases in the composite catalyst. This viewpoint was further supported by the analyses of Fourier transformed (FT) k^3 -weighted EXAFS spectra for Co/CoN_x-CNT as shown in Figure 3b. The first peak at 1.32 Å can be identified as the $Co-N_x$ moieties, which evidently proved the presence of Co single atoms in the composite catalyst. The Co-N_x coordination was found slightly shorter than 1.38 Å of the Co-N₄ moiety in CoPc, suggesting a relatively strong Co coordination environment in the composite catalyst. The second pronounced peak at 2.18 Å was ascribed to the Co-Co coordination as pure Co foil, which thus confirmed the predominantly formation of metallic Co nanoparticles in Co/CoNx-CNT. Overall, results of our XAFS measurement were consistent with the HAADF-STEM observations and provided evidence for the presence of both Co single atoms and Co nanoparticles in the composite catalyst. The results were successfully published in Journal of Materials Chemistry A in 2022. (Part C(8) ref 2)



Figure 3 a) XANES and **b)** Fourier-transformed (FT) EXAFS spectra of Co/CoN_x-CNT-33-800T at Co K-edge. Relevant cobalt phthalocyanine (CoPc), and Co foil were used as references.

6.2 Potential for further development of the research and the proposed course of action (*Maximum half a page*)

Inspired by the above example, we synthesized a series of bifunctional Co catalysts with high metal loading (25 wt%) by a facile one-pot pyrolysis method, such as Co/Cu, Co/Mn and Co/Mo. The metal ions were pre-mixed with dicyandiamide (C₂H₄N₄) via N coordination with the use of ball milling equipment, followed by a series of carbonization steps at 600-800°C. For Co NPs supported on CNT with atomically dispersed CoN₄ moiety was obtained with Mn as the 2nd metal. For Co and Cu pair, bimetallic NPs with atomically dispersed single metal catalysts on CNT were obtained. For Co and Mo pair, Co-MoC_x catalyst was obtained. Interestingly, while Co-Cu showed exceptional reactivity towards ammonia borane hydrolysis (more than double the rate for Pure Co catalyst), it showed inferior activity in HER. On the other hand, Co-MoC_x showed sluggish reaction rate towards ammonia borane hydrolysis, but showed exceptional good activity in alkaline hydrogen evolution reaction. Cyclic voltammetry showed that it has a relatively high electrochemically active surface area (ECSA) of 477.25 mF/cm² (which is comparable to the Ru SACs materials) and a specific surface area of 56.4 m²/g. The η_{10} was found to be 130 mV (Figure 4a) with a Tafel slope of 156.08 mV/dec (Figure 4b), which is comparable to Pt SACs supported on mesoporous carbon matrix. Obviously, the synergistic effect of the two different neighboring metals are different, leading to exceptional activities towards different reaction types. The results were successfully published in New Journal of Chemistry in 2023 (Part C(8) ref 3, attached in this report).



Figure 4 a) HER polarization curves of electrocatalysts, b) the corresponding Tafel plots for different electrocatalysts.

7. Layman's Summary

(Describe <u>in layman's language</u> the nature, significance and value of the research project, in no more than 200 words)

This project focuses on developing catalysts for hydrogen production. The researchers investigated a specific material called ammonia borane, which has the potential to store and release hydrogen gas, and in an effort to find a catalyst that is efficient, cost-effective, and stable for the hydrolysis of ammonia borane to generate hydrogen. A method was developed to create a carbon nanotube material containing cobalt nanoparticles and atomically dispersed cobalt single-atoms. This unique structure prevented the nanoparticles from aggregation into lumps, maintaining their catalytic activity. The presence of the single atoms also enhanced the adsorption of water molecules, facilitating the hydrolysis process. The results showed that when the ratio of cobalt to the carbon material was carefully controlled, the catalyst exhibited excellent reactivity and stability, outperforming most other catalysts used for ammonia borane hydrolysis. The hydrogen generation rate achieved was significantly high, and the catalyst remained durable even after multiple cycles of use. This research addresses the need for efficient and affordable catalysts for hydrogen production. By utilizing both nanoparticles and single-atoms, it was demonstrated that synergistic effect improved the overall performance of the catalyst. Such advancements are crucial for the development of hydrogen-based technologies and the realization of a sustainable energy economy.

Part C: Research Output

8. Peer-Reviewed Journal Publication(s) Arising <u>Directly</u> From This Research Project (*Please attach a copy of the publication and/or the letter of acceptance if not yet submitted in the previous progress report(s).* All listed publications must acknowledge RGC's funding support by quoting the specific grant reference.)

The	e Latest Stat	us of Public	ations		Title and Journal / Book				
Year of Publication	Year of Acceptance (For paper accepted but not yet published)	Under Review	Under Preparation (optional)	Author(s) (denote the correspond- ing author with an asterisk*)	(with the volume, pages and other necessary publishing details specified)	Submitted to RGC (indicate the year ending of the relevant progress report)	Attached to this Report (Yes or No)	Acknowledged the Support of RGC (Yes or No)	Accessible from the Institutional Repository (Yes or No)
2021	2022	N/A	N/A	Poon, PC.; Wang, Y.; Li, W.; Suen, D.WS.; Lam, W.W.Y.; Yap, D.Z.J.; Mehdi, B.L.; Qi, J.; Lu, XY.; Wong, E.Y.C*; Yang, C.*; Tsang, CW.*	Synergistic effect on ammonia borane hydrolysis by Co catalysts with atomically dispersed CoN _x active sits for hydrogen generation, <i>Journal of</i> <i>Visualized</i> <i>Experiment</i> <i>s</i> 2021 , doi: 10.3791/62 965.	Yes (2022)	No	Yes	Yes
2022	2022	N/A	N/A	Poon, PC.; Lee, KM.; Wang, Y.; Lam, W.W.Y.; Leung, P.SW.; Lu, XY.; Li, W.; Mehdi, B.L.; Lu, Y.; Tsang, CW*; Wong, E.Y.C.*	Synthesis of metal nanoparticl es supported on carbon nanotube with doped Co and N atoms and its catalytic application s in hydrogen production, <i>Journal of Materials</i> <i>Chemistry</i> <i>A</i> 2022, 10, 5580-5592.	Yes (2022)	No	Yes	Yes
2023	2023	N/A	N/A	Shen, W.; Suen, D.WS.; Sze	Co–MoC _x supported on N-doped CNTs for	No	Yes	Yes	Yes

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		Е.ТР.;	efficient		
		Chen, X.*;	hydrogen		
		Liang, C.;	evolution		
		Tsang,	reaction		
		CW.*	under		
			alkaline		
			medium		
			conditions.		
			New		
			Journal of		
			Chemistry		
			2023 , <i>47</i> ,		
			21024 -		
			21032,		
			doi:10.103		
			9/d3nj0393		
			7d.		

(a) are my trained students at THEi, responsible for the rate measurement of the catalytic hydrolysis of ammonia borane.

(b) are the research assistants at THEi, responsible for the syntheses, structural characterizations and the rate measurement of the catalytic hydrolysis of ammonia borane.

(c) are the partners from University of Liverpool, responsible for the HAADF-STEM analyses for the proof of presence of single atoms in the catalysts.

(d) are the colleagues at THEi, responsible for the ICP

measurement for metal contents.

(e) **Expression of the research partner from Heng Sang University of Hong Kong,** responsible for the feasibility of the technological commercialization.

(f) are the partners from Sun Yat-Sen University and Dalian University of Technology, responsible for EXAFS and XANES analyses.

(g) are student, associate professor and professor, respectively, at Dalian University of Technology and are my research partners, responsible for the electrolysis experiments.

(h) **Example 1** is research partners from Metropolitan University of Hong Kong, responsible for structural characterization.

9. Recognized International Conference(s) In Which Paper(s) Related To This Research Project Was / Were Delivered

(*Please attach a copy of each conference abstract*)

Month / Year /	TT: 41 -	Conformer Norma	Submitted to RGC (indicate the year ending of the relevant progress	Attached to this Report	Acknowledged the Support of RGC	Accessible from the Institutional Repository
Place	Title	Conference Name	report)	(Yes or No)	(Yes or No)	(Yes or No)

2021	Fabrication of Carbon-Based Single-Atom Catalysts using Pyrolytic Decomposition of g-C ₃ N ₄ for Hydrogen Energy Production	The 6th International Conference on New Energy and Future Energy Systems (NEFES 2021), 1-4 Nov 2021	Yes (2022)	Yes	Yes	No
2022	Synergistic function of nanocluster and single atom catalysts for exceptional performance in the hydrogen production from solid hydrogen storage materials	Recent Advances in Chemistry, UK, 8-9 Dec 2022	No	Yes	Yes	No
2022	A Feasibility Assessment of the Optimal Use of Hydrogen Drones in Fashion Item Replenishment Logistics	International Association of Maritime Economists Conference 2022 in Busan, Korea, 14-16 Sept 2022, Virtual conference	No	Yes	Yes	No

10. Whether Research Experience And New Knowledge Has Been Transferred / Has Contributed To Teaching And Learning

(Please elaborate)

- 1. Shared new findings during HKIE Technical Seminar, Topic: Meeting the Hydrogen Economy era: Recent Advances in H_2 Production & Storage Technology on 17 Oct 2022.
- 2. Shared new findings during HKIE training course on environmental and energy issue, 23 Mar 2023.
- 3. Introduced the hydrogen research to HKPC colleague on 16 May 2022.
- 4. Gave a research seminar on hydrogen energy research in a Innocarnival 2022 held at THEi on 12 Oct 2022.
- 5. Presented a hydrogen research talk at the Research Symposium help at THEi on 29 March 2022.
- 6. Presented a public research talk at the Hong Kong Institute of Environmentalists, topic: Meeting the Hydrogen Economy era: Development of Hydrogen Production Method from Hydrogen Storage Materials, on 26 March 2022.
- Served as Technical Committee Chair on Hydrogen Energy, at the 5th International Conference on Power and Energy Applications (ICPEA2022) during Nov 18-20, 2022 in Guangzhou.
- 8. Published a video publication on Journal of Visualized Experiements, with topic: Synergistic effect on ammonia borane hydrolysis by Co catalysts with atomically dispersed CoN_x active sits for hydrogen generation in 2021. (Part C(8) ref 3)

11. Student(s) Trained

(Please attach a copy of the title page of the thesis) (Cover pages attached in this report)

Name	Degree Registered for	Date of Registration	Date of Thesis Submission / Graduation
	Environmental		
	Engineering &	Sept 2018	June 2021/Dec 2021
	Management		
	Environmental		
	Engineering &	Sept 2017	June 2021/Dec 2021
	Management		
	Environmental		
	Engineering &	Sept 2017	June 2021/Dec 2021
	Management		
	Environmental		
	Engineering &	Sept 2018	June 2022/Dec 2022
	Management		
	Environmental		
	Engineering &	Sept 2018	June 2022/Dec 2022
	Management		
	Environmental		
	Engineering &	Sept 2020	June 2022/Dec 2022
	Management		
	Environmental		
	Engineering &	Sept 2020	June 2022/Dec 2022
	Management		
	Environmental		
	Engineering &	Sept 2020	June 2024/Dec 2024
	Management		

12. Other Impact

(e.g. award of patents or prizes, collaboration with other research institutions, technology transfer, teaching enhancement, etc.)

- 1. Collaboration developed with determination of the Co single atom by HAADF-STEM technique.
- 2. Collaboration developed with the construction of the second state of the second state of the determination of the coordination environment of Co single atom by Synchrotron Radiation technique.
- 3. Collaboration with Hang Seng University hydrogen-powered drone development.

13. Statistics on Research Outputs

Peer-reviewed Journal	Conference Papers	Scholarly Books,	Patents Awarded	Other Research Outputs
Publications	_	Monographs		(please specify)
		and		

			Chapters			
No. of outputs	3	3	N/A	N/A	Туре	No.
arising directly					N/A	N/A
from this						
research						
project						

14. Public Access Of Completion Report

(Please specify the information, if any, that cannot be provided for public access and give the reasons.)

Information that Cannot Be Provided for Public Access	Reasons			
N/A	N/A			