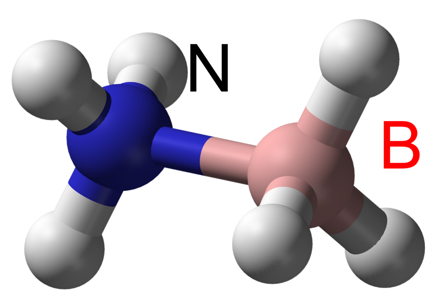
A novel catalyst with highly stable and atomically dispersed cobalt and manganese nitride nanocluster active sites for hydrolytic release of hydrogen from ammonia borane

Mr YAN Yujie, BSc (Hons) in Green Engineering & Sustainability,
Department of Construction, Environment, & Engineering
Supervisor: Ir Dr Alex TSANG, Assistant Professor

Abstract
The development of low-cost, highly efficient and durable catalysts is the key to the practical use of ammonia borane (NH_3BH_3, AB) as a promising storage material for on-board hydrogen production. Atomically dispersed metal supported catalysts not only maximize the efficiency of metal utilization but also serve as a robust support for metal nanoparticles. Herein, we report a facile synthesis of a type of carbon nanotube (CNT) that consists of both $CoMn_4$ nanocluster (NC) and atomically dispersed cobalt & manganese single-atoms supported on carbon materials. Our results indicated that $CoMn_4$ NCs were successfully embedded within the layers of graphitic carbon to effectively prevent them from aggregation and loss of catalytic activity. In addition, the Co and Mn single atoms catalysts (SACs) greatly lowered the adsorption barriers of water molecules onto the catalysts for fast hydrolysis of AB. Interestingly, the best reactivity and stability towards AB hydrolysis were achieved: with the highest specific H_2 generation rate reach up to 8372 mLH_2 ·gCoMn·min^{-1} at 40^{o}C, which surpassed most of the non-noble metal catalysts for AB hydrolysis to date. The current study presents an example of how nanoclusters and single-atoms can be synergistically exploited for heterogeneous catalysis applications.



Ammonia borane
(NH_3BH_3, AB)

Background
Ammonia borane (AB) has garnered significant interest as a hydrogen storage material due to its high H_2 content (approximately 19.6% by weight) and favorable thermodynamic properties. This compound can release H_2 via thermal decomposition or chemical reactions, making it a potential candidate for clean energy applications, especially in fuel cells.
The *key features* of ammonia borane include:

1. **High H_2 Density:** Its high H_2 storage capacity makes it efficient compared to other materials.
2. **Stability:** AB is extremely stable at r.t., which simplifies handling and storage.
3. **H_2 Release Mechanisms:** H_2 can be released from AB through processes such as pyrolysis, where heat is applied, or by reacting with precious metal catalysts to facilitate the release at lower temperatures.

Objectives
1. To devise low-cost metal catalysts to release H_2 from AB by experimental methodology, which is comparable to precious metal catalysts.
2. To optimize the low-cost metal catalysts using theoretical approach.
3. To confirm the identity of the low-cost metal catalysts by physicochemical methods.

Methodology & Results
By direct carbonization of a mixture of cobalt- and manganese-containing precursors and melem-C_3N_4 at 800^{o}C, nanoclusters $CoMn_4$ catalysts supported on Co-Mn SACs-embedded CNT was synthesized as shown in **Figure 1**. It was found that when the ratio of Co to Mn was 2:1, optimal reactivity was obtained, as shown in **Figure 2**. (rate: 8372 mLH_2 ·gCoMn·min^{-1} at 40^{o}C).

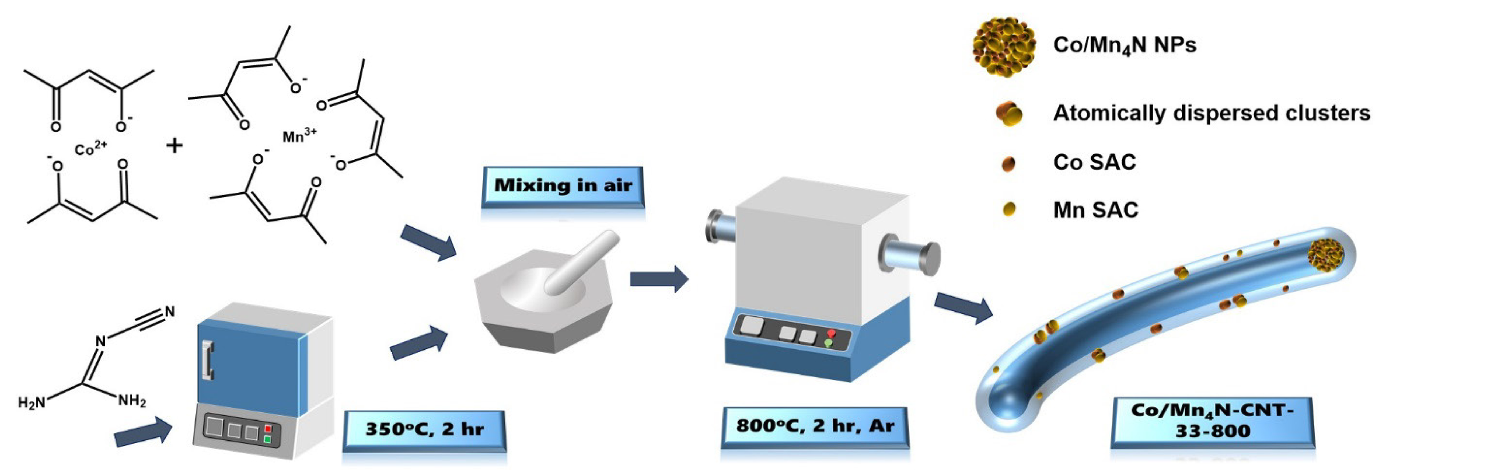


Figure 1. Schematic diagram of the in-situ synthesis of $CoMn_4N$/Co-Mn-N_x-CNT-200-800 via a calcination method.

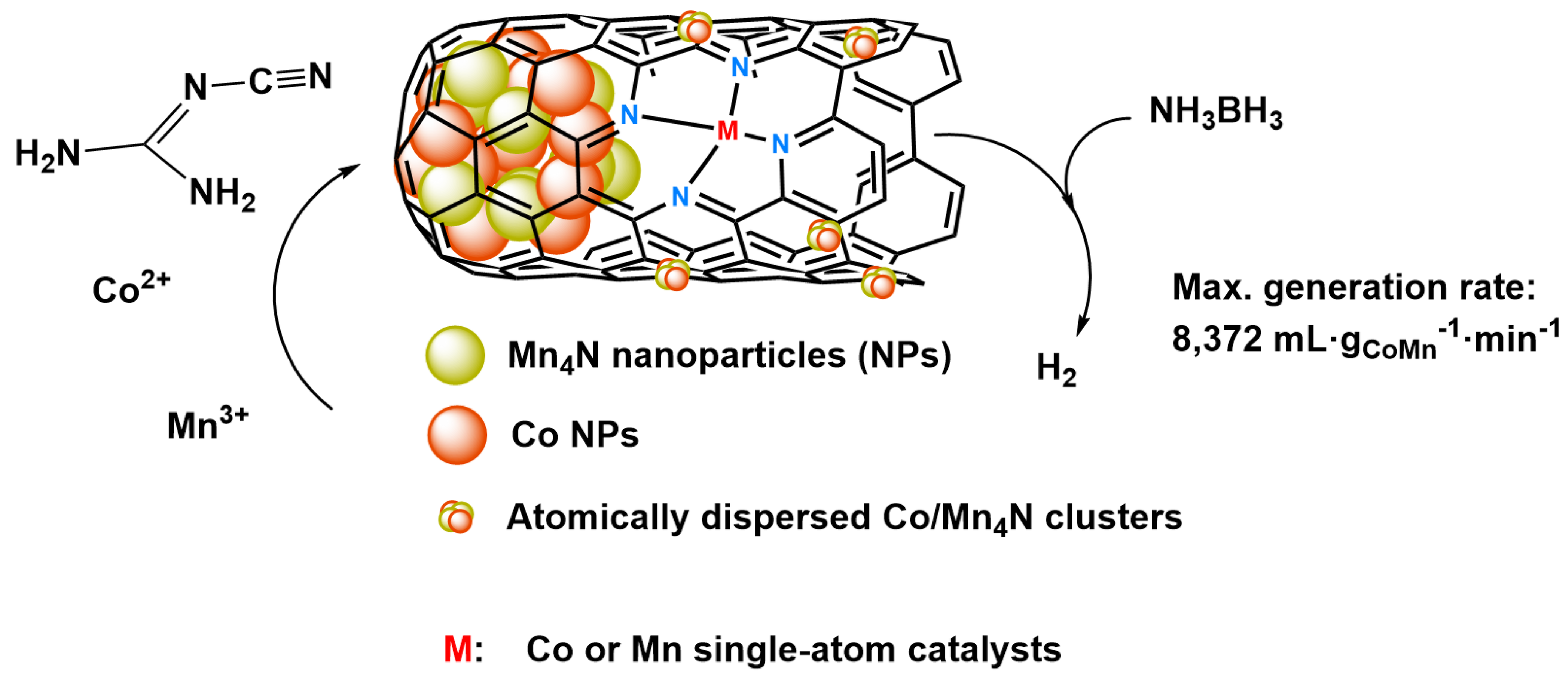


Figure 2. $CoMn_4N$/Co-Mn-N_x-CNT-200-800 displayed a maximum effective H_2 generation rate of 8372 mL_{H2}·$g_{CoMn}$$^{-1}$·min^{-1}.

Catalyst Characterization
The carbon nanotube structure of the catalyst was unequivocally proved by advanced spectroscopic techniques, such as HAADF-STEM, as shown in **Figure 3**.

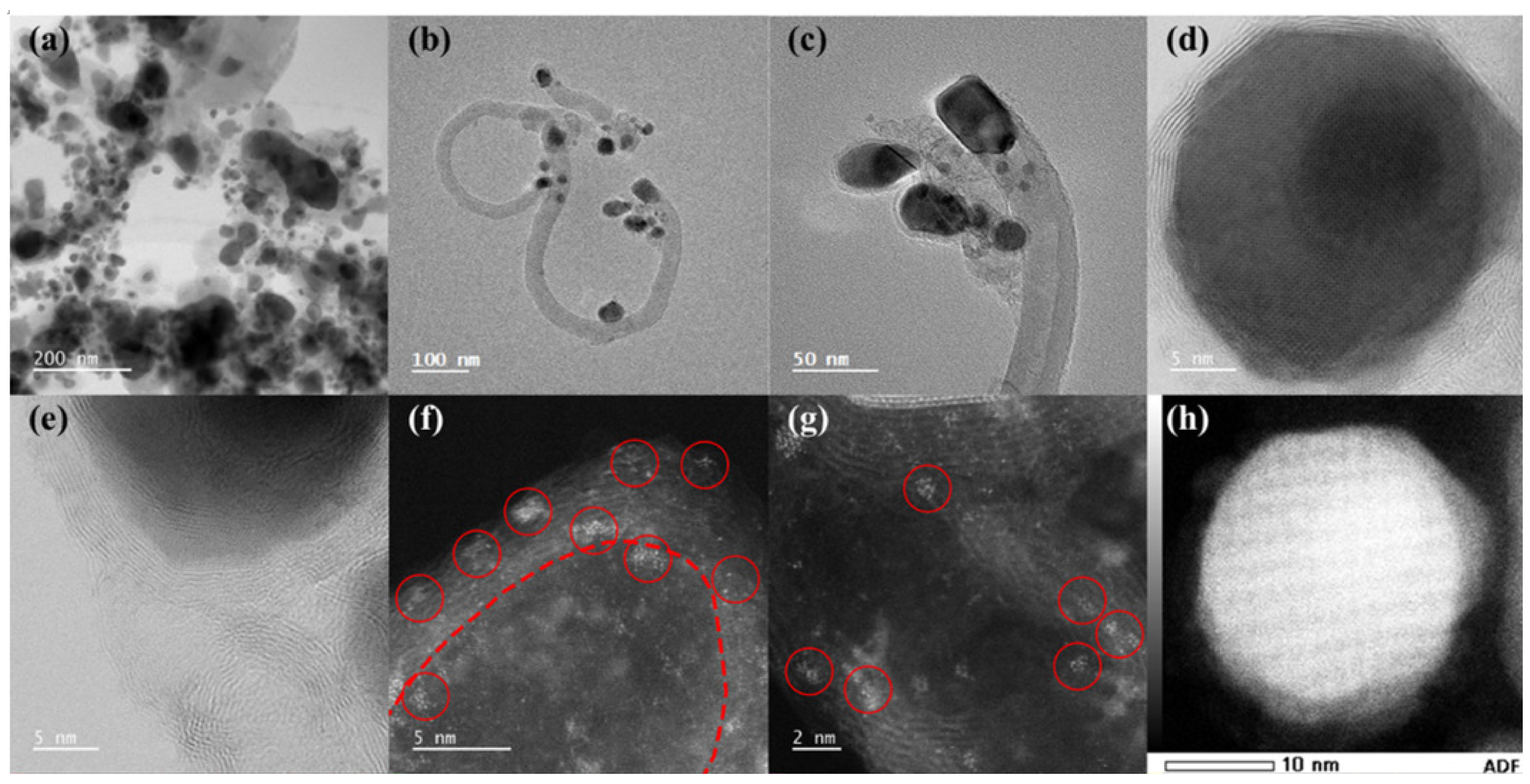


Figure 3. HAADF-STEM images the $CoMn_4N$/Co-Mn-N_x-CNT-200-800 catalyst showing (a) various sizes of NPs; (b) CNT containing and surrounded by NPs; (c) magnified portion of the CNT; (d) a NP with a diameter of ~22 nm; (e) layers of graphitic C on an NP; (f, g) nanoclusters (circled in red); (h) ADF image.

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Research Output: Suen, D.W.-S.; Yan, Y.; Wong, E.Y.-C.; Lu, X.-Y.; Chen, J.; Tsang, C.-W.; Yang, C.; Ouyang, S. A novel catalyst featuring highly stable cobalt and manganese nitride nanoclusters dispersed on single atom-anchored carbon nanotubes for hydrolytic release of hydrogen from ammonia borane. *Surfaces and Interfaces* **2025**, 106519, doi:10.1016/j.surfin.2025.106519.