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2018 DOE Hydrogen and Fuel Cells Program Review:

Methane Pyrolysis for Base-Grown Carbon Nanotubes and CO_2-free H_2 over Transition Metal Catalysts

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Pacific Northwest National Laboratory
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Project ID
h2045

U.S. DEPARTMENT OF ENERGY

Overview

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Timeline

- Project Start Date: 4/15/18
- Project End Date: 10/15/19
- Total Project Budget: $750K

Project started **<u>April 15, 2018</u>**

Budget

- Total Project Budget: $750K
  - Total Recipient Share: $375K
  - Total Federal Share: $375K
  - Total DOE Funds Spent*: $0

    * As of 3/31/18

Barriers

A. Reformer Capital Costs and Efficiency

Reduce criteria and other emissions from H_2 production from natural gas

Target: $2/kg Hydrogen Production

Partners

- Pacific Northwest National Laboratory
- C4-MCP, LLC
- Southern California Gas Company
- West Virginia University

Relevance

- **Objective**: Develop a new process for producing **CO_2-free hydrogen** and **solid carbon** from inexpensive and domestically available natural gas and reduce the net production cost of **H_2 to < $2/kg** with the sale of valuable byproduct carbon.
  - Development and use of co-products from hydrogen production
  - Carbon nanotubes produced via “base-growth” versus “tip-growth” mechanism, the conventional technology, offers potential for economic advantage.
  - Low cost H_2 production is relevant to H2@Scale

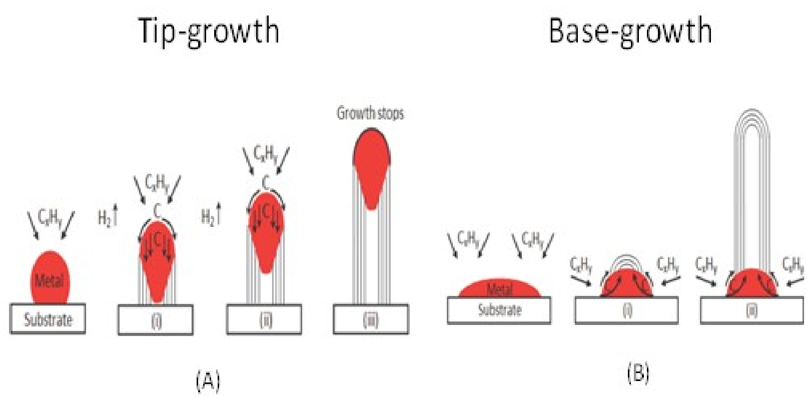

Illustration of (A) tip-growth and (B) base-growth carbon nanotube formation. This technology uses the more desirable base growth process.

Approach

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- **Background**: West Virginia University reported a promising new catalyst innovation for methane conversion to CO_2-free hydrogen and solid carbon nanotubes produced via "base growth" mechanism offering potential for catalyst regenerability and high carbon product purity.
- **Approach**: Build upon this prior research and:
  - Improve catalyst design.
  - Develop the reactor engineering enabling a commercially viable process technology.
  - Understand the produced carbon characteristics and market potential.
  - Evaluate the overall techno economics.

Date	Milestones
7/15/2018	Set-up methane pyrolysis experimental test stand apparatus, develop test protocol, and obtain required experimental testing permits.
10/15/2018	Evaluate at least 10 different catalysts and select candidate formulation with highest conversion for harvesting and characterization studies. Report on ability to achieve >50% single pass conversion.
1/15/2019	Determine catalyst regeneration and preliminary harvesting protocol conditions. Target at least 5 regeneration cycles, and with <10% activity loss if possible.
4/15/2019	Characterize candidate catalysts using a least 3 techniques (e.g., TEM, TPR, and BET) in order to better understand reaction mechanism.
7/15/2019	Characterize at least three carbon products produced from candidate catalyst(s) using at least 3 techniques to understand materials properties.
10/15/2019	Update TEA to determine process efficiency and CAPEX and OPEX cost. Report on ability to achieve a projected H2 cost <$2/kg at a 25 kg/day scale.

Accomplishments and Progress

Catalyst Developed for CNT Production – WVU Results

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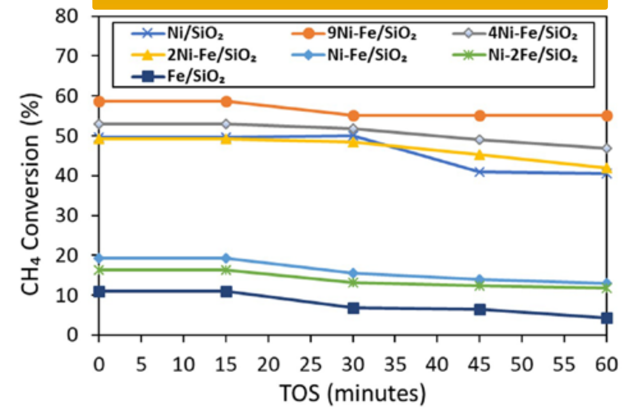
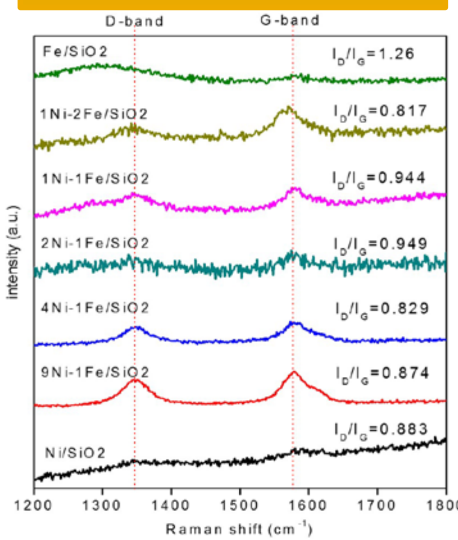
$$CH_4 \rightarrow C(s) + 2H_2 \quad \Delta H^o = 74.8 \text{ kJ/mol}$$

- Ni/Fe/Co catalysts developed for methane pyrolysis; metal consistency key catalyst design variable
- Alloy formation of bimetallic catalysts were observed in **H_2-TPR** analysis.
- **XRD** showed that Ni content in the bimetallic catalyst controls the degrees of graphitization of the formed
- The degree of crystallinity (I_D/I_G) of CNT was calculated using **Raman** analysis.

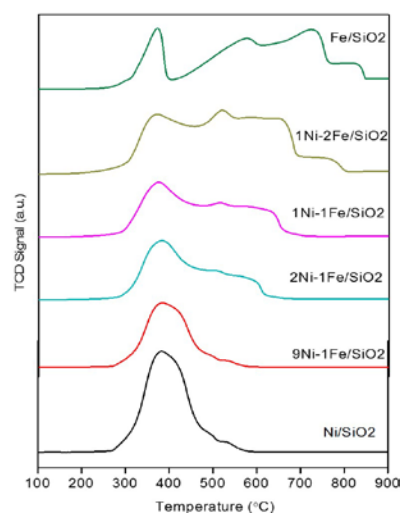
Catalytic Performance



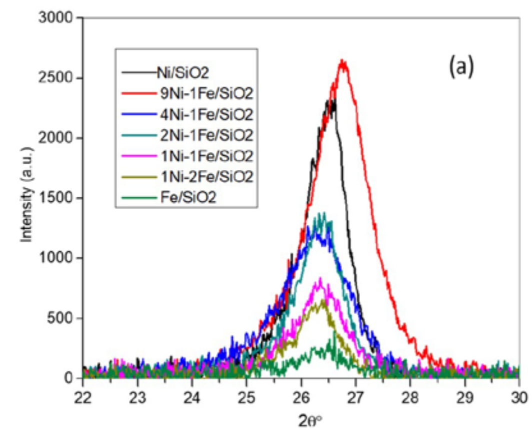
Raman Spectra of CNT



TPR of fresh catalysts



XRD pattern of CNT



CNTs produced via "base growth" versus "tip growth" mechanism – WVU Results

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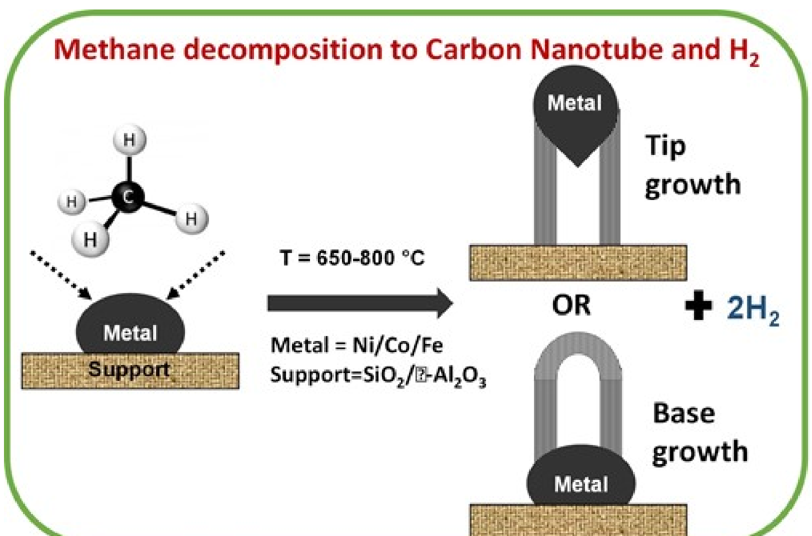
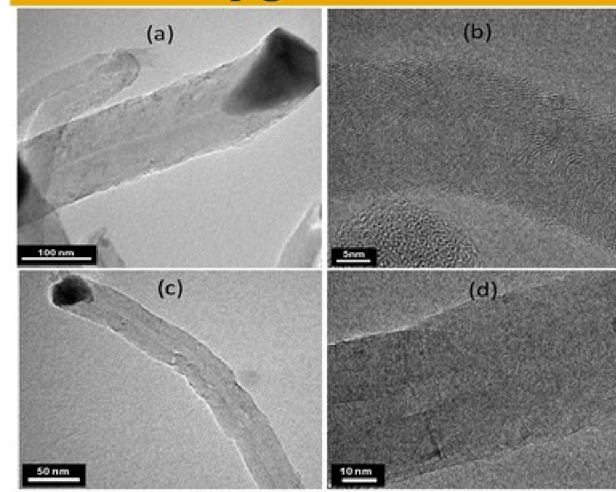
- TEM analysis helped to understand the different morphologies of the CNT.
  - Diameter, wall type, and growth mechanism on different catalysts determined
- Catalyst developed which facilitates "base" versus "tip" growth mechanism.
- "Base" grown CNTs offer potential for catalyst regeneration and higher carbon product purity.

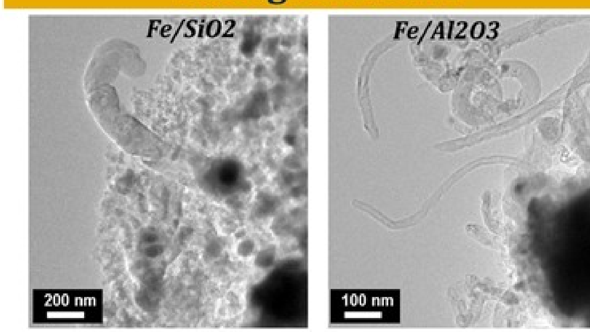


Tip grown CNT



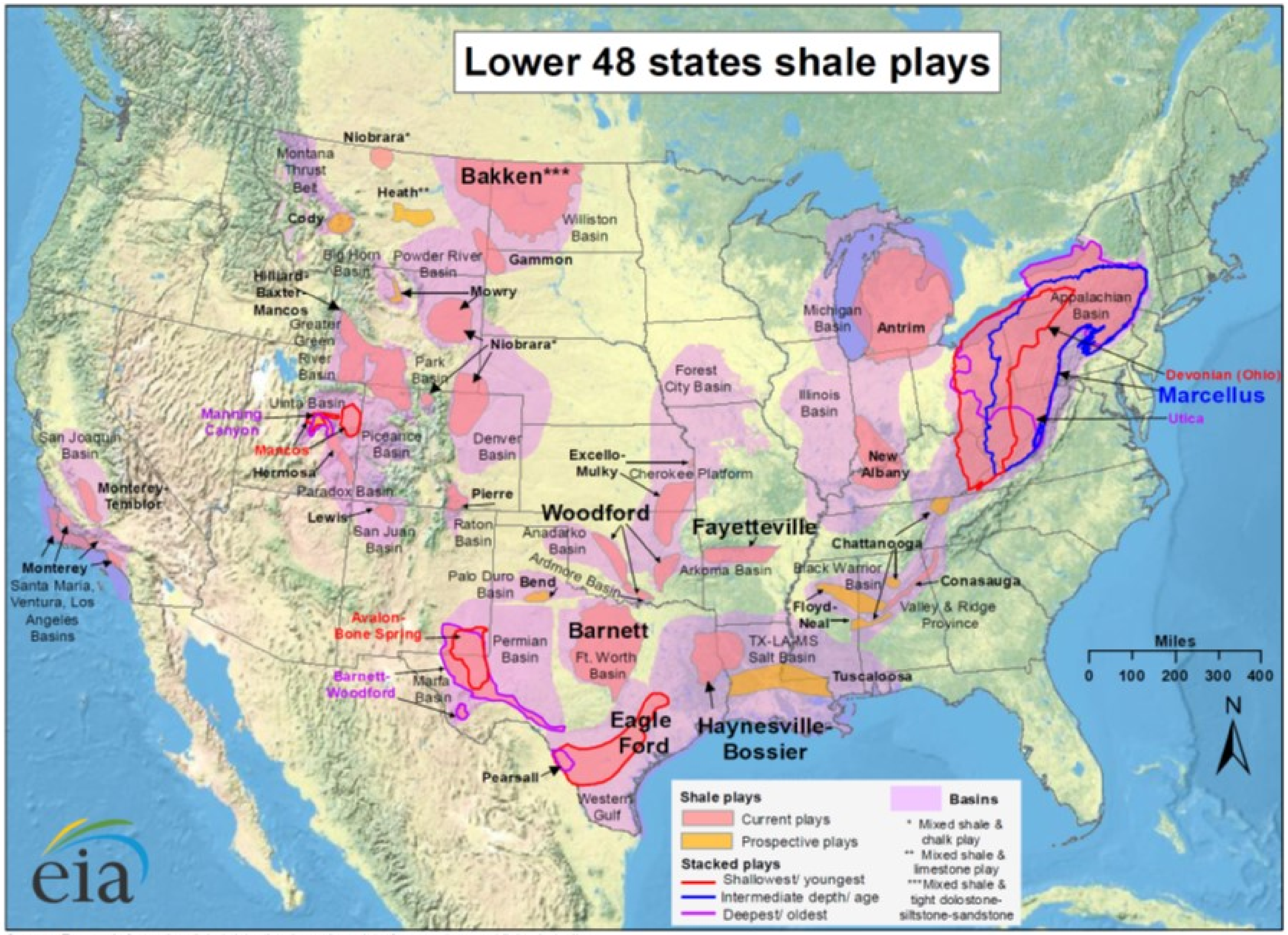
TEM images of CNT formed over (a,b) 9Ni-1Fe/SiO_2, (c,d) 9Ni-1Co/SiO_2, T = 650 °C, TOS = 60 minutes, GHSV = 42000h^{-1}

Base grown CNT



TEM images of CNT formed over Fe/SiO_2 and Fe/Al_2O_3, T = 700 °C, TOS = 60 minutes, GHSV = 42000h^{-1}

Accomplishments and Progress
Location and Projected Reserves for Major U.S. Shale Gas Basins in the United States



Source: Energy Information Administration based on data from various published studies.
Updated: May 9, 2011

Accomplishments and Progress

Market Analysis for Potential Carbon Products (K= thousand, M= million, MT= metric ton)

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Type of Carbon	Types of Applications	Expected Price for Carbon	Size of the Market (current/ projected)	Corresponding Hydrogen Production[(a)]
Carbon black [79,80,81]	Tires, printing inks, high-performance coatings and plastics	$0.4–2+ /kg depending on product requirements	U.S. market • ~ 2M MT (2017) Global market • 12M MT (2014) • 16.4M MT (2022)	U.S. market • 0.67M MT Global market • 4M MT (2014) • 5.4M MT (2022)
Graphite [82]	Lithium-ion batteries	$10+/kg	Global market • 80K MT (2015) • 250K MT (2020)	Global market • 27K MT (2015) • 83K MT (2020)
Carbon fiber [83,84,85]	Aerospace, automobiles, sports and leisure, construction, wind turbines, carbon-reinforced composite materials, and textiles	$25–113/kg depending on product requirements	Global market • 70K MT (2016) • 100K MT (2020)	Global market • 23.3K MT (2016) • 33.3K MT (2020)
Carbon nanotubes [86,87]	Polymers, plastics, electronics, lithium-ion batteries	$0.10–600.00 per gram depending on application requirements	Global market • 5K MT (2014) • 20K MT (2022)	Global market • 1.7K MT (2014) • 6.7K MT (2022)
Needle coke [88]	Graphite electrodes for electric arc steel furnaces	~$1.5/kg	Global market • ~1.5M MT (2014)	Global market • ~0.50M MT (2014)

(a) Based on stoichiometric ratio of carbon to hydrogen present in methane. Does not take into account process efficiency or use of hydrogen to provide process heat or loss of hydrogen during hydrogen recovery.

R. Dagle et al. "R&D Opportunities for Development of Natural Gas Conversion Technologies for Co-Production of Hydrogen and Value-Added Solid Carbon Products", Technical Report, PNNL-26726, ANL-17/11, 2017.

Break-Even Price of Carbon Products vs. the Cost of Methane as a Percentage of the Revenue from the Sale of Hydrogen and Carbon Products, as Functions of the Price of Methane. Price of H_2 = $4/kg

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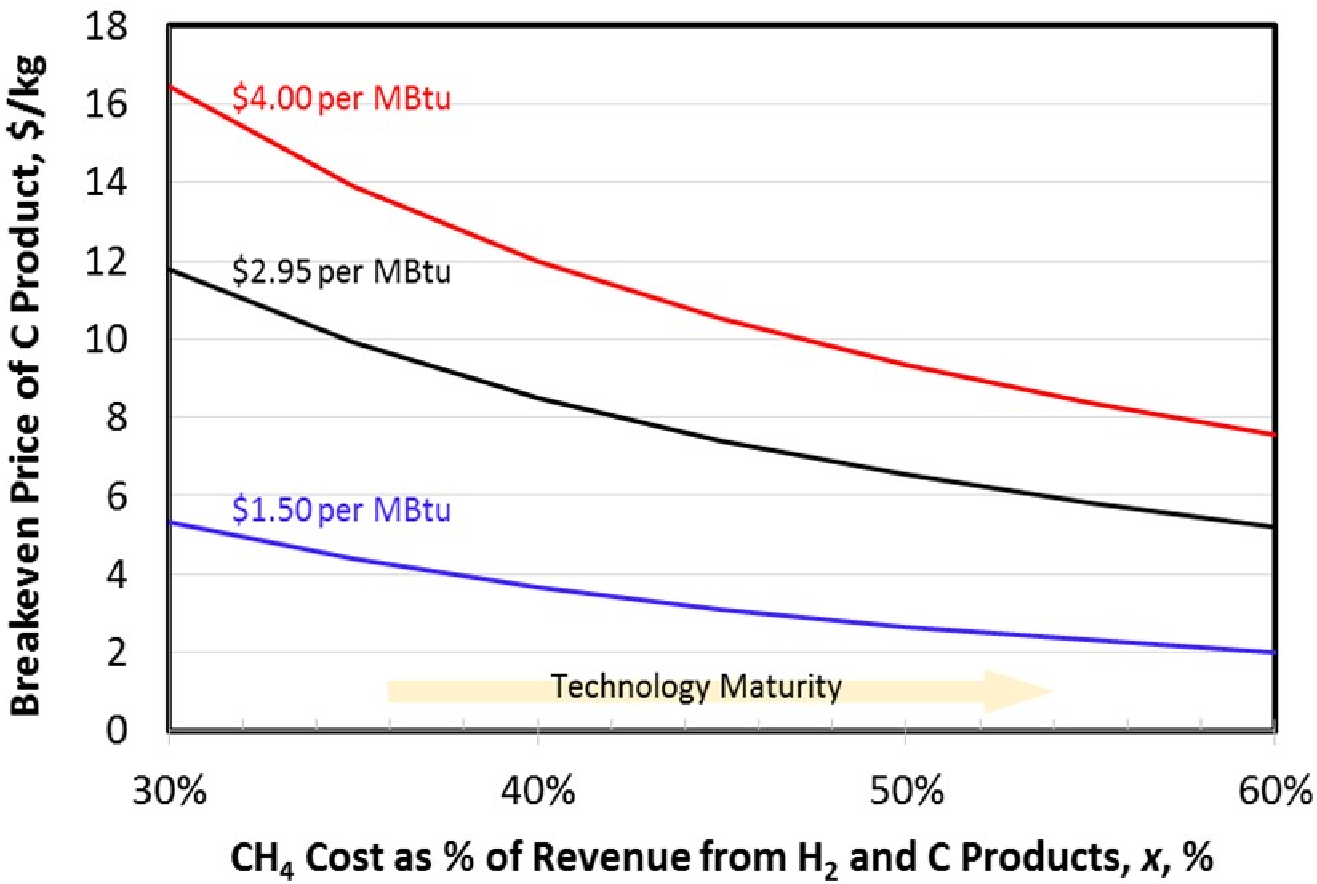

Analysis by Shabir Ahmed (ANL), as reported in “R&D Opportunities for Development of Natural Gas Conversion Technologies for Co-Production of Hydrogen and Value-Added Solid Carbon Products,”, Technical Report, PNNL-26726, ANL-17/11, 2017.

Collaboration & Coordination

Partner	Project Roles
C4-MCP, LLC	Management lead, project coordination, tech-to-market plan
Pacific Northwest National Laboratory	Techno economic analysis, bench-scale reactor processing, catalyst design, carbon harvesting and characterization
West Virginia University	Catalyst synthesis and performance evaluations, and characterization
Southern California Gas Company	Sponsor, industrial advisor, stakeholder

- C4-MCP, LLC is a company specifically created to commercialize technology for the conversion of natural gas to hydrogen and solid carbon products.
- SoCalCas has a strong interest in using their natural gas infrastructure to mitigate emissions of greenhouse gases (GHG) and local criteria pollutants.
  - California's mandates significant GHG, NO_x, and particulate matter emission reductions.
  - Converting natural gas or biogas to H_2 while simultaneously producing high-value carbon materials as described in this project may represent a cost-effective means of decarbonizing H_2 production.
  - Supporting the use of fuel cells in electric vehicle and distributed power generation markets by providing low-cost hydrogen could substantially reduce, NOx, and particulate emission.

Future Work

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- Further improve catalyst design for CNT versus amorphous carbon production
- Develop processing for carbon harvesting and catalyst regeneration and reuse
- Characterize produced CNTs and understand market potential
- Develop flow sheet for envisioned commercial process
- Techno economic evaluation
- Tech-to-market plan

Critical Assumptions

Assumption	Validation or Mitigation
Carbon harvesting via physical separation/agitation technique is suitable for catalyst/CNT separation (FCC type reactor)	Validation: Evaluate assumption on physical separation feasibility via bench scale reactor experimentation. Mitigation: Evaluate alternative acid wash technique known in the literature to separate CNTs; evaluate impact of additional cost on economics
Value and/or market size of produced CNTs is sufficient to enable favorable economics	Validation: Evaluate techno economics via model. Mitigation: Evaluate upgrading of produced CNTs to more valuable product (e.g., carbon fibers) and assess additional cost in techno economic model
Produced CNTs versus amorphous carbon ratio is high enough to yield sufficient valuable product	Validation: Evaluate techno economics via model. Mitigation: Develop research approach to design catalyst for increased CNT/amorphous carbon product ratio (research execution would likely require additional scope).

Summary

Project Start: April 15, 2018

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- **Objective**: Develop a new process for producing **CO_2-free hydrogen** and **solid carbon** from inexpensive and domestically available natural gas and reduce the net production cost of **H_2 to < $2/kg** with the sale of valuable byproduct carbon.
- **Relevance**: H2@Scale project for development and use of co-products from hydrogen production.
- **Approach:** Build upon innovative catalytic material reported at West Virginia University (WVU) and:
  - Improve catalyst design.
  - Develop the reactor engineering enabling a commercially viable process technology.
  - Understand the produced carbon characteristics and market potential.
  - Evaluate the process techno economics.
- **Accomplishments**: Catalyst developed at WVU for carbon nanotube production produced via “base growth” versus “tip growth” mechanisms which offers potential for catalyst regenerability and high product purity
- **Collaboration:**
  - Pacific Northwest National Laboratory
  - West Virginia University
  - C4-MCP, LLC
  - Southern California Gas Company