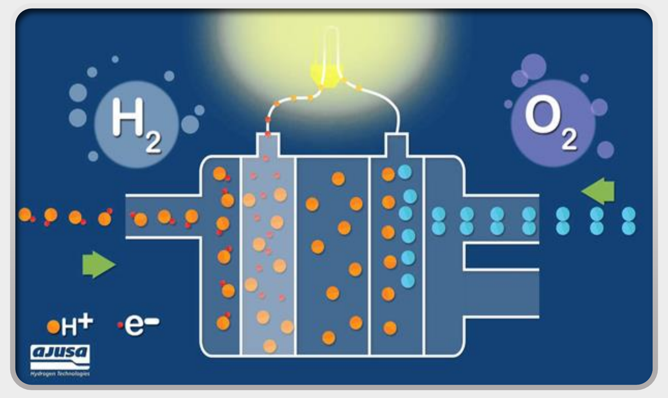
Nitrogen modified Titanium Dioxide (N-TiO_2) Promotes Carbon Monoxide Oxidation over Copper Catalysts

Guoqiang Cao, Nan Yi

Department of Chemical Engineering, University of New Hampshire, Durham, NH, USA

Background

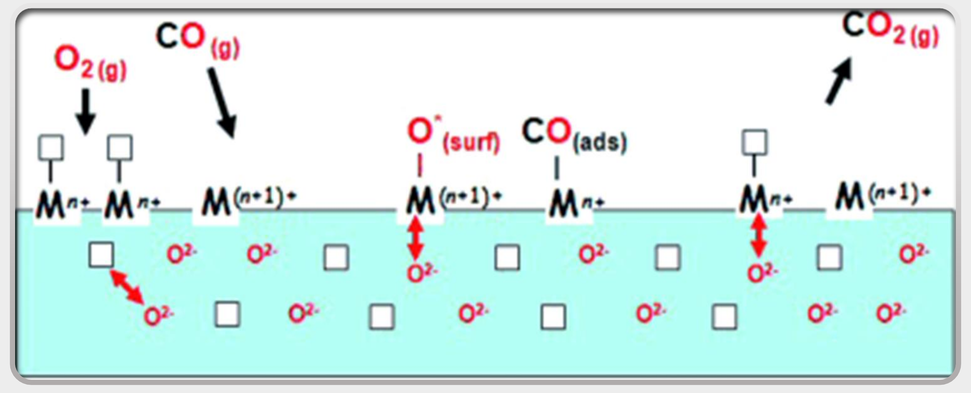


Toxic Carbon Monoxide

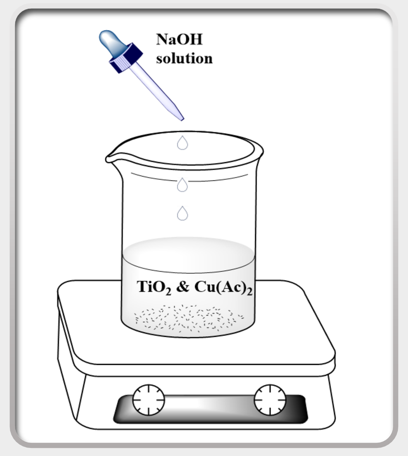
- Poisoning of anodes in PEMFCs [1]
- Seriously harmful to human body

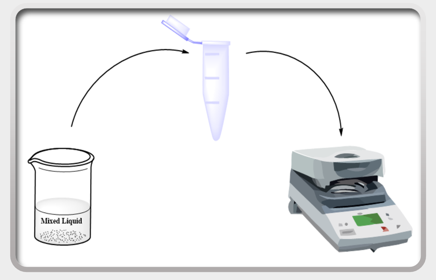
Carbon Monoxide Oxidation

- Cost-effective and robust catalysts are desirable [2]



Catalyst Preparation





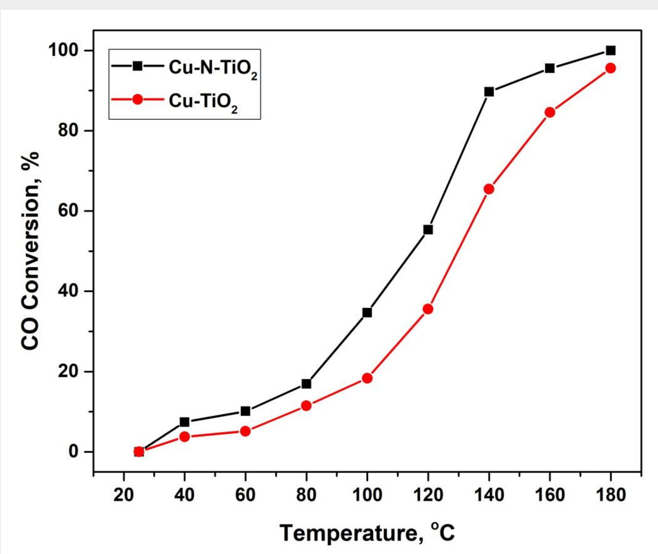
Directly formation of CuO from Cu(Ac)$_2$ and NaOH[3]

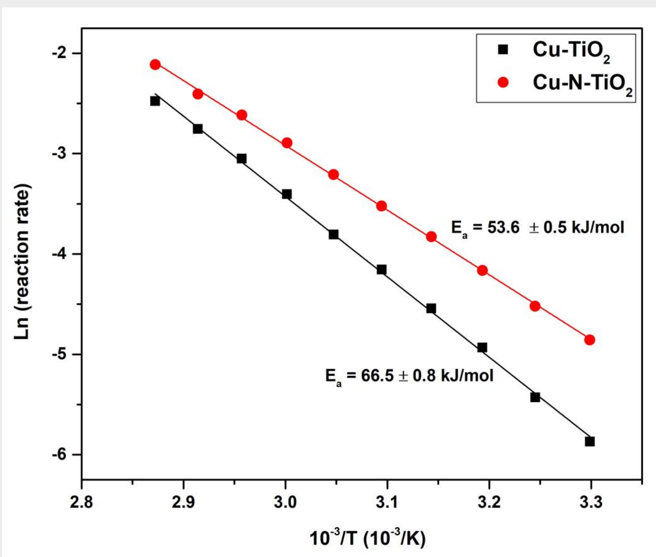
Cu(CH$_3$COO)$_2$ + 2NaOH ➡ CuO

Cu-N-TiO_2: Designed copper loading as 10 weight %

- Synthesis of N-TiO_2 support
  - Urea and TiO_2 physically mixed with ratio of 5 : 1 and vacuum dried
  - Mixed Urea and TiO_2 Calcined at 550 °C for 15 h to obtain N-TiO_2 support
- Loading Cu through wet impregnation method
  - Molar ratio of Cu(Ac)$_2$ to NaOH = 1 : 4, stirred in D.I. water for 1 h
  - After the centrifugation, precipitates were centrifuged and vacuum dried

Catalytic Activity





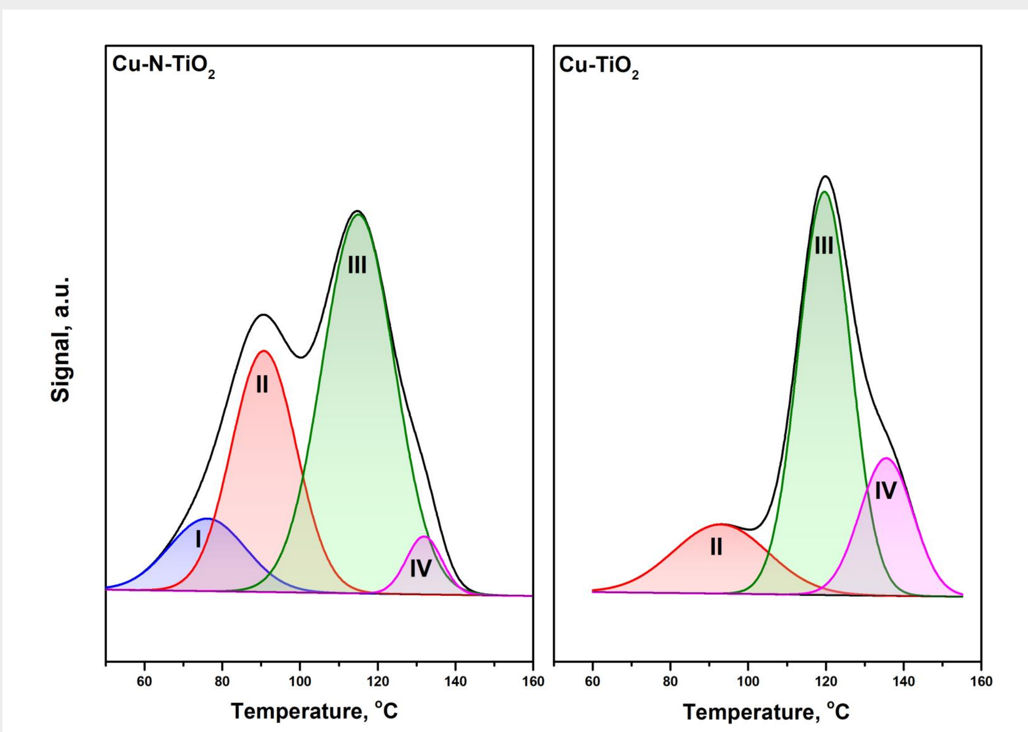
Cu-N-TiO_2 with introduced nitrogen shows better activity

- CO conversion (%)
  - Cu-N-TiO_2, has the higher CO conversion than Cu-TiO_2
- Activation Energy
  - Cu-N-TiO_2, showed lower activation energy

Conditions

- Pretreated under Helium at 200 °C for 1.5 h
- Gas: 1% CO/ 20% O_2 /He
- Flow rate: 30 ml/min
- 50 mg sample
- Heating rate: 5 °C/min

Temperature Programmed Reduction (TPR)



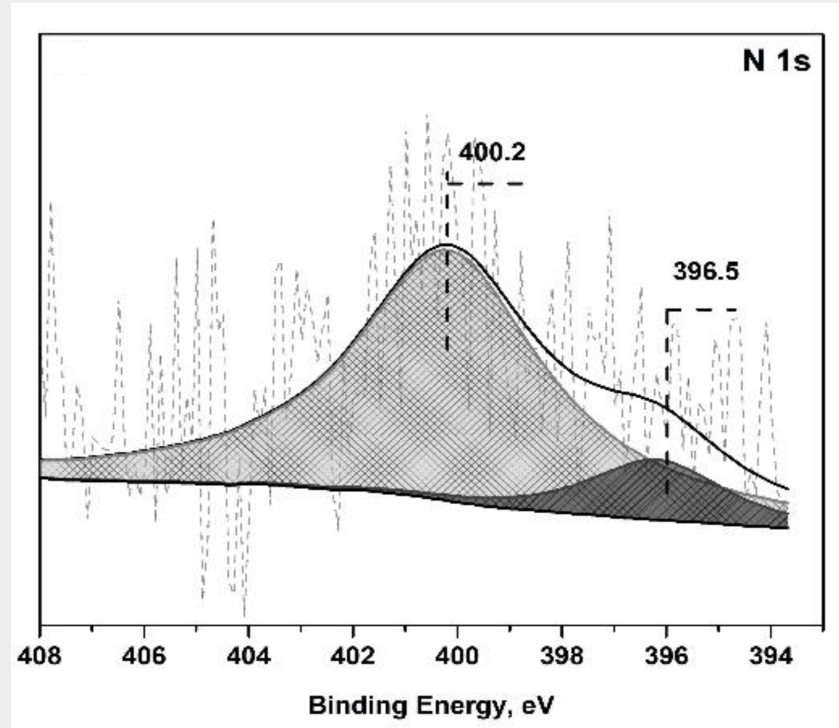
Conditions

- Pretreated under pure Helium at 200 °C for 1.5 h
- Gas: 10% H_2 /Ar, Flow rate: 30 ml/min
- 50 mg sample, Heating rate: 5 °C/min

- **Unique peak around 76 °C existed for Cu-N-TiO_2**
- **90% hydrogen consumption of Cu-N-TiO_2 resulted from lower temperature reduction (lower than 120 °C)**
- **18.8% of hydrogen was consumed under 120 °C for Cu-TiO_2 sample**

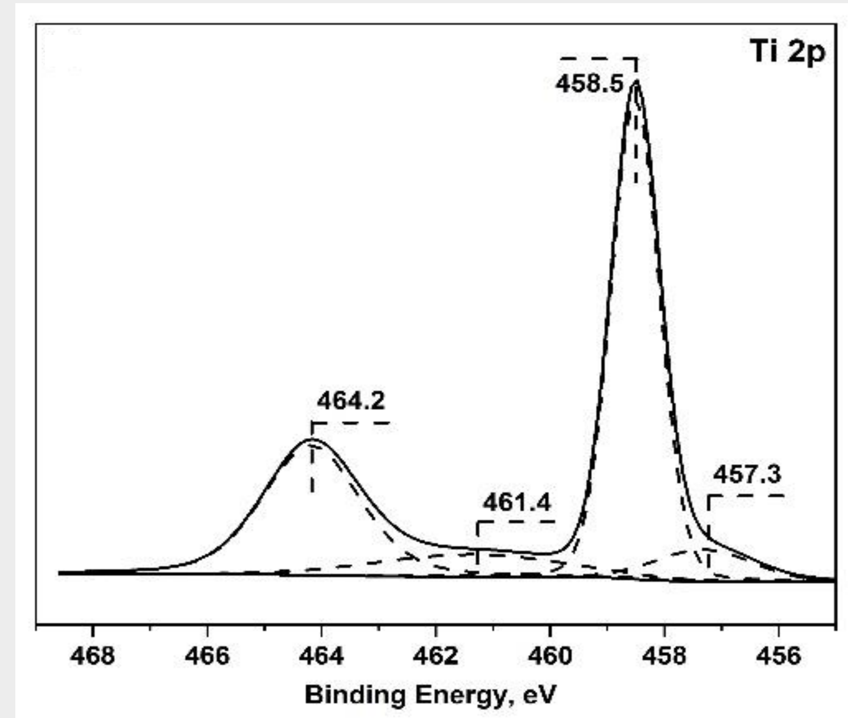
Sample	T (°C) Hydrogen Consumption (μmol/gcata) (%)							
	Peak I		Peak II		Peak III		Peak IV	
Cu-N-TiO_2	76	186.0 (12.4)	90	431.1 (28.8)	115	735.4 (49.2)	132	142.1 (9.5)
Cu-TiO_2			93	270.2 (18.8)	120	829.4 (57.8)	136	334.6 (23.3)

X-ray Photoelectron Spectroscopy (XPS)



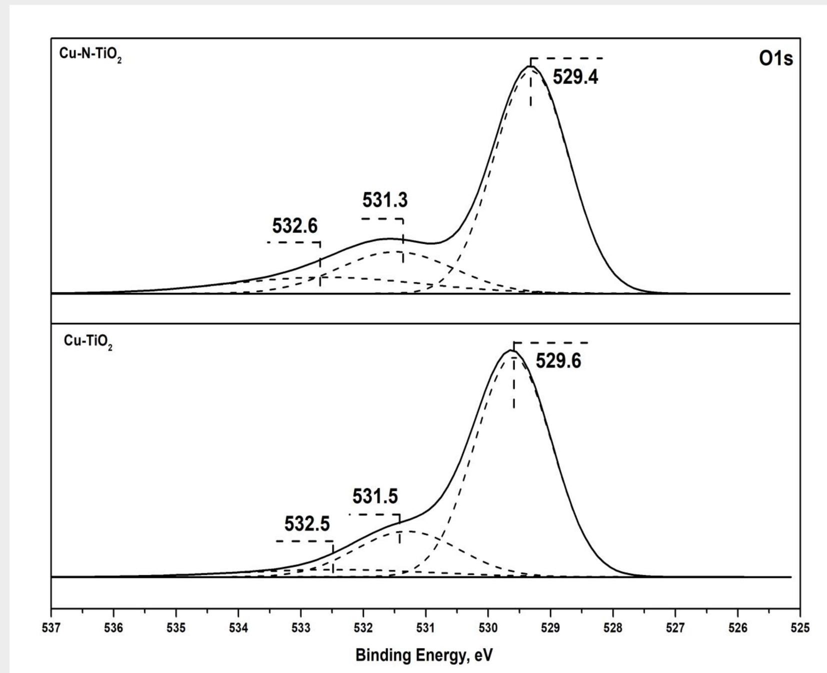
Two forms of nitrogen existed

- 400.2 eV is attributed to interstitial nitrogen
- 396.5 eV, typically represents substitutional nitrogen



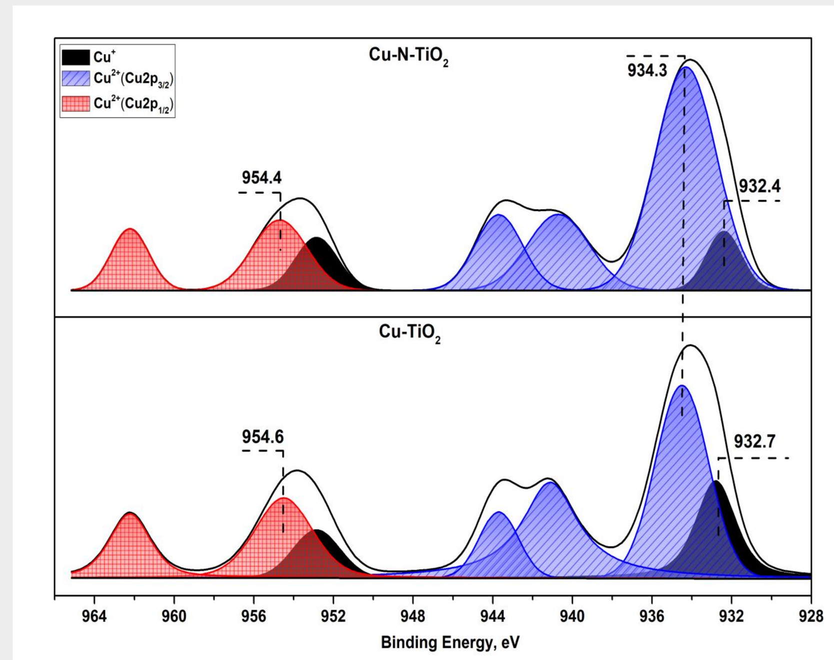
Only N-TiO_2 has Ti^{3+}

- 457.3 eV and 461.4 eV are attributed to Ti^{3+} species
- 458.5 eV and 464.2 eV represents Ti^{4+} species



Similar amount of O_{surf}

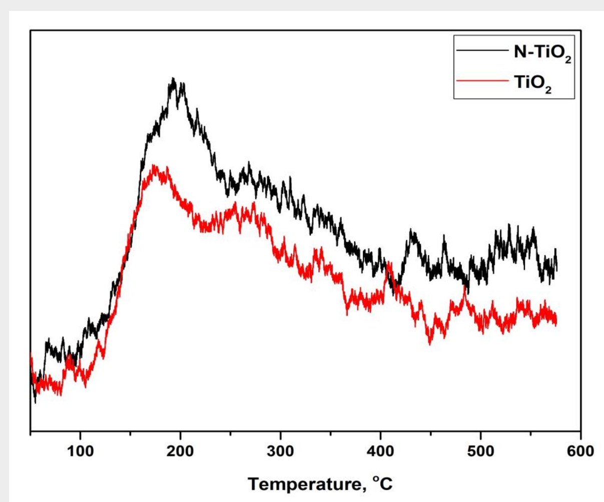
- 529.4 eV is attributed to O_{latt}
- 531.3 eV is assigned as O_{surf}
- 532.6 eV presented O_{ad}



Cu-N-TiO_2 has less amount of Cu^+

- 932.4 eV is attributed to Cu^{1+} species
- 933.7 eV, typical Cu 2p binding energy, represents Cu^{2+} species

Oxygen Storage Capacity (OSC)



Nitrogen promoted OSC of support

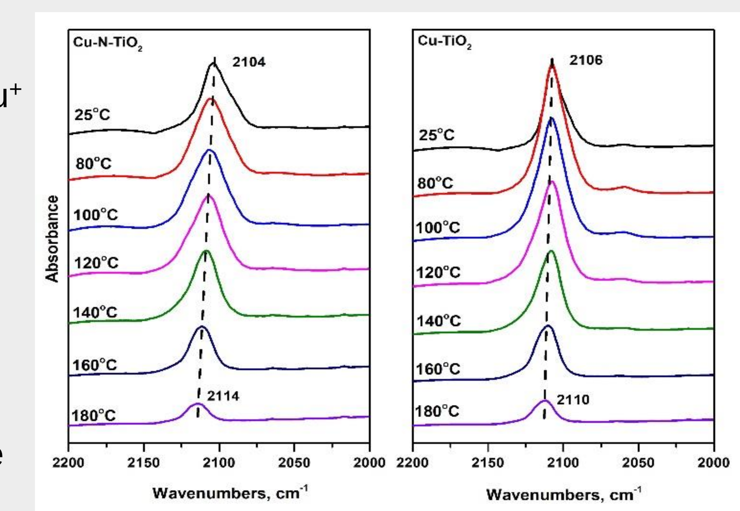
- N-TiO_2 support showed 28.9% higher than that of TiO_2

In-situ DRIFTS

- 2104 ~ 2114 cm^{-1} : CO-Cu^+ bond
- Band shift appears more dominant over Cu-N-TiO_2

Conditions

- Gas: 1% CO/ 20% O_2 /He
- Flow rate: 30 ml/min



Summary

- Nitrogen modified copper-titanium dioxide catalysts showed better catalytic performance on CO oxidation than Cu-TiO_2.
- Both interstitial and substitutional nitrogen are observed on the surface, but the interstitial nitrogen is the dominant nitrogen species.
- The enhancement of reaction rate could be attributed to the improved copper dispersion.
- It was proposed to correlate the reaction rate with the value of ([Cu^+]/[O]$_{sur}$) while considering the vanity around active copper species

References

[1] Ajusa Hydrogen Technologies, 2018.

[2] S. Royer, D. Duprez, Catalytic Oxidation of Carbon Monoxide over Transition Metal Oxides, ChemCatChem, 2011, 1, 24.

[3] T. Kida, T. Oka, M. Nagano, Y. Ishiwata, X. G. Zheng, Synthesis and Application of Stable Copper Oxide Nanoparticle Suspensions for Nanoparticulate Film Fabrication, J. Am. Ceram. Soc, 2007, 90, 107-110.

Acknowledgements

- Department of Chemical Engineering, University of New Hampshire
- Summer Teaching Assistant Fellowship from Graduate School, University of New Hampshire
- Center for Nanoscale Systems, Harvard University