BOROCARBONITRIDES:

METAL FREE ELECTROCATALYST FOR ELECTROCHEMICAL REDUCTION OF CO_2

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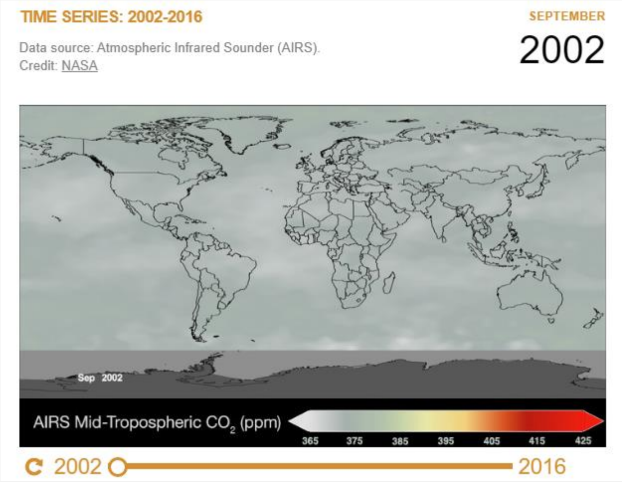
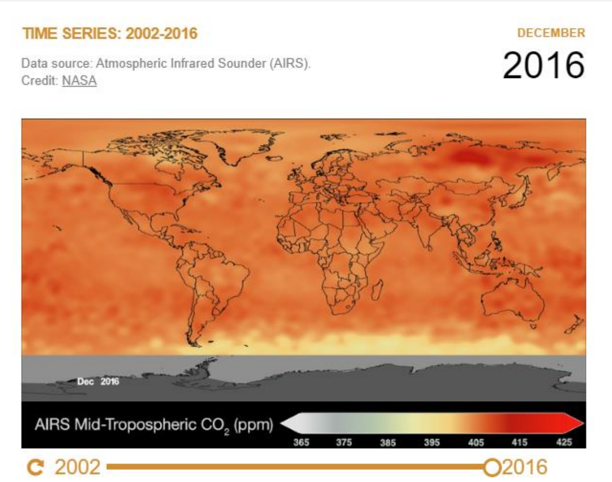
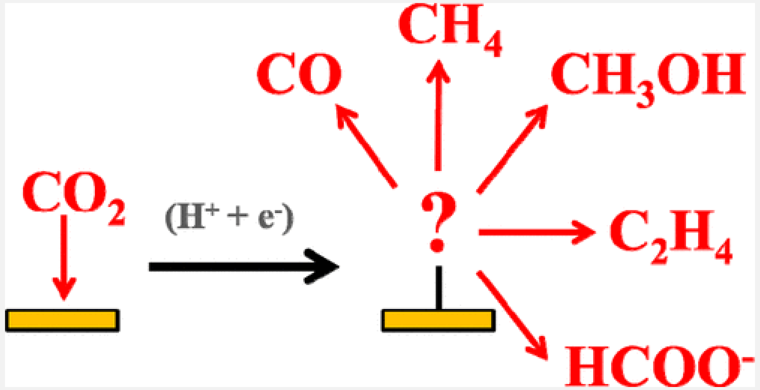
Introduction

- Rising atmospheric CO_2 levels has drastic effects on the climate of earth
- Electrochemical reduction of CO_2(ECO2RR) is an effective approach to reduce atmospheric CO_2 levels and convert CO_2 into value added fuels





- Metals are widely studied but they suffer with drawbacks such as high cost and undesirable competing HER
- Carbon-based materials offer an alternative approach
- Pristine carbon materials are inert towards ECO2RR, doping with heteroatoms such as N can alter the properties which renders carbon active towards ECO2RR
- In this work we study the effect of doping B and N in activated charcoal



Possible reduction products in ECO2RR

Borocarbonitrides : Synthesis and Characterization

- Borocarbonitride synthesized by high temperature reaction of activated charcoal, urea and boric acid
- Composition of B and N in carbon can be altered by changing the amounts of reactant
- BCN exhibit high specific surface area and a high CO_2 uptake in comparison with undoped activated charcoal

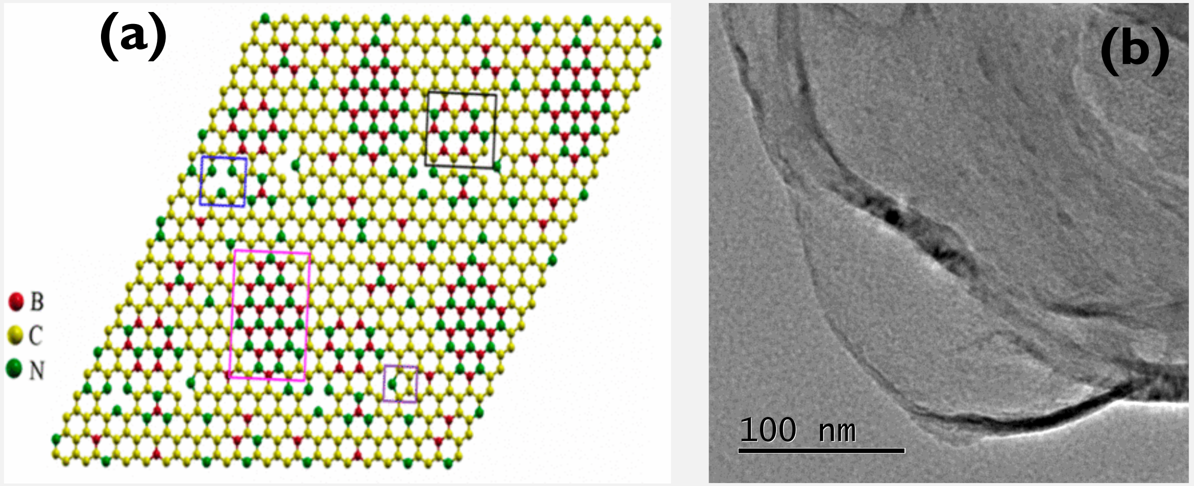


Figure 1: (a) Schematic structure of BCN, (b) TEM image

H_3BO_3 + $CO(NH_2)_2$ + C → $B_xC_yN_z$

BCN-1
BCN-2
BCN-3
BCN-4

Increasing B,N content

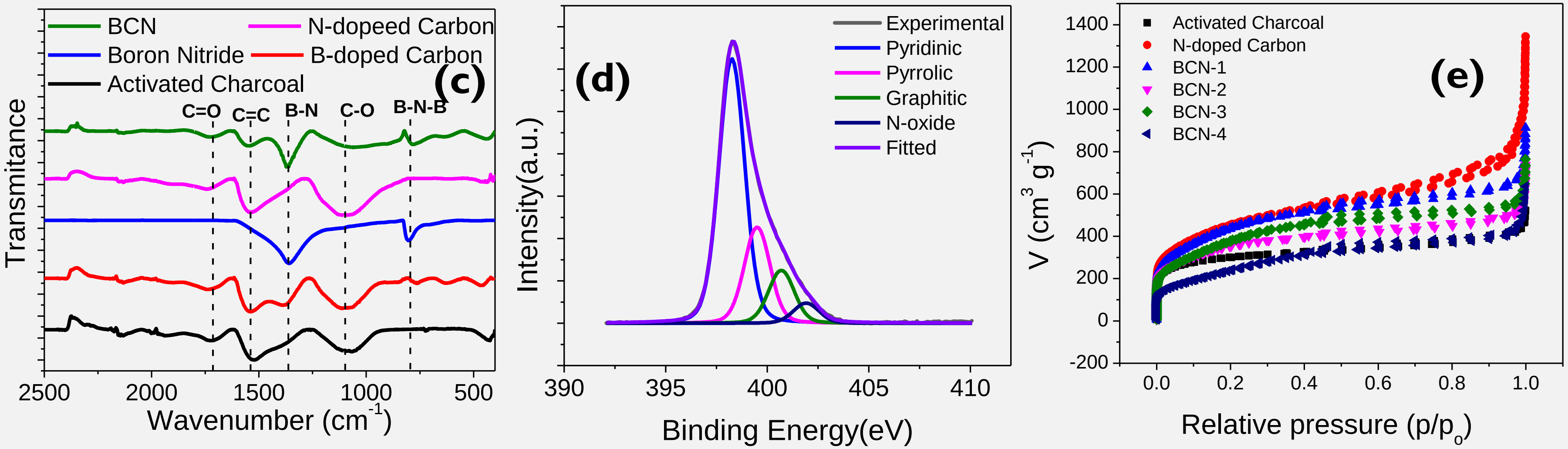


Figure 1:(c) FTIR spectra showing nature of bonds in BCN, (d) Nature of N defects in BCN, (e) N_2-adsorption isotherms

Electrochemical Activity

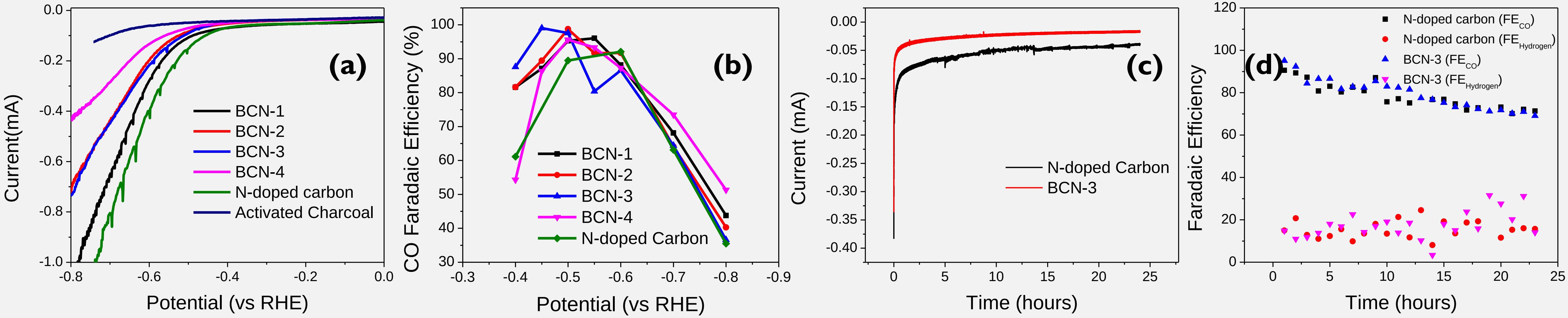


Figure 2: (a) LSV (b) FE_{CO} as a function of potential, (c) constant potential electrolysis and (d) FE_{CO} over 24 hours

- Electrochemical activity of BCN was studied in an aqueous bicarbonate electrolyte with continuous CO_2 purging
- BCN reduces CO_2 to form CO as the only product
- BCN-3 exhibits highest **FE_{CO} of 99% at -0.45V** in comparison of N-doped carbon which reaches a maximum **FE_{CO} of 92% at -0.6V**
- BCN is more stable than N-doped carbon

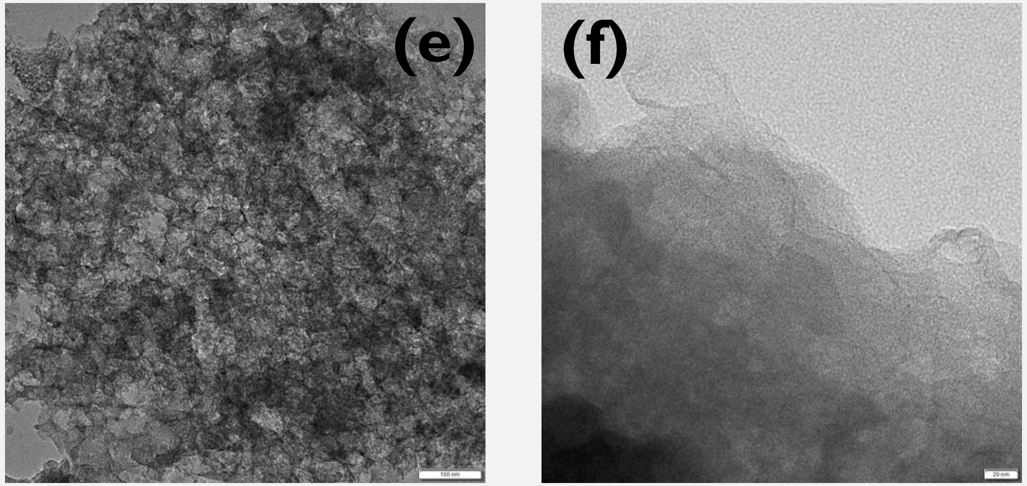
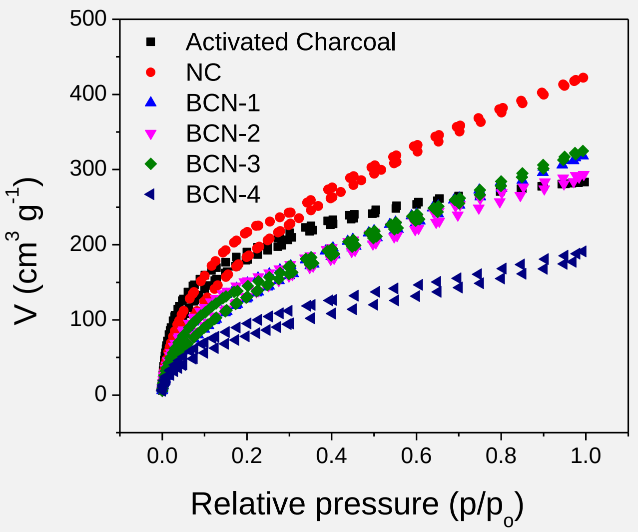


Figure 2: TEM image of (e) N-doped carbon and (f) BCN after 24 hours of constant potential electrolysis

Understanding Electrochemical Activity

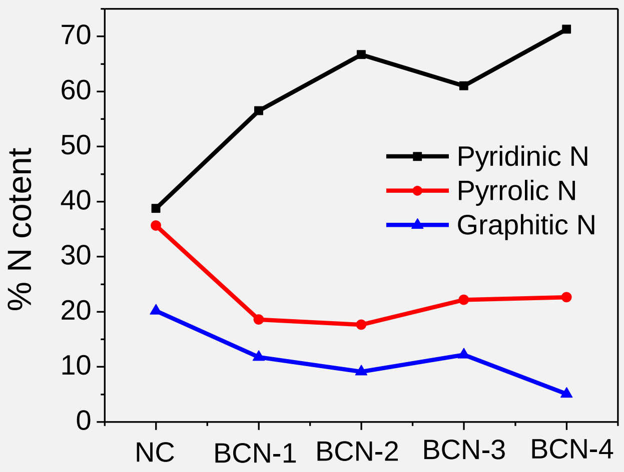
Electrochemical Reduction of CO_2 on catalyst surface

Adsorption of CO_2



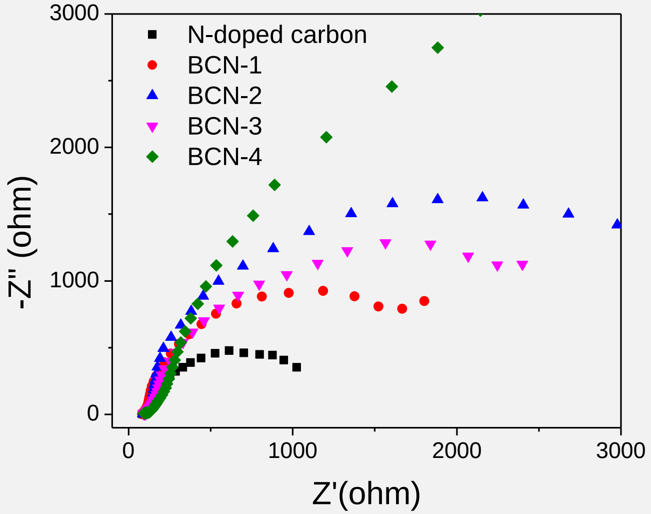
- Doped carbons; BCN and NC all exhibit higher CO_2 uptake than AC
- Among BCN, BCN-3 exhibits highest CO_2 uptake of 14.5 mmol/g

Catalytic center



- DFT studies suggest that pyridinic N site is most favorable for ECO2RR followed by pyrrolic and graphitic
- BCN has higher concentration of pyridinic N site compared to NC

Rate of electron transfer



- NC has lowest charge-transfer resistance
- Charge transfer resistance increases with increase BN content due to insulating BN domains

Conclusion

- N-sites are the active center for ECO2RR in N-doped carbon, but reaching a high doping levels of N is difficult
- Incorporation of Boron with Nitrogen in carbon lattice leads to the formation of borocarbonitrides, where the content of B,N can be tuned and a high doping levels can be achieved
- Borocarbonitrides reduce CO_2 to CO in aqueous bicarbonate electrolyte
- Concentration of pyridinic N site is higher in BCN which is responsible for efficient ECO2RR
- BN domains in BCN impart structural stability to the catalyst

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2. Raidongia, K., Nag, A., Hembram, K. P. S. S., Waghmare, U. V., Datta, R., & Rao, C. (2010). BCN: a graphene analogue with remarkable adsorptive properties. *Chemistry–A European Journal*, *16*(1), 149-157.

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