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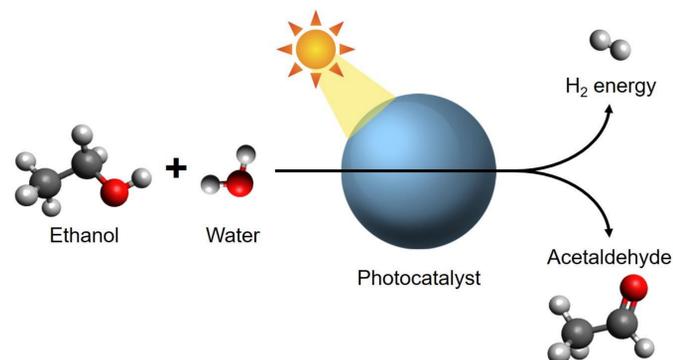
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## Background

- Photoreforming has been shown to improve H<sub>2</sub> evolution rate due to the favourable organic oxidation.<sup>1</sup>
- Selective photoreforming can produce H<sub>2</sub> energy and valuable organic products simultaneously.<sup>2,3</sup>
- Ethanol from waste biomass is an attractive substrate for the sustainable co-production of H<sub>2</sub> and acetaldehyde.
- Carbon nitride has received significant attention in the area of selective photoreforming due to its well-positioned band edges for H<sub>2</sub> evolution reaction and selective oxidation.<sup>4,5</sup>
- However, the application of carbon nitride is limited by its poor photocatalytic performance.
- Hence, a simple and effective engineering of carbon nitride for enhanced selective ethanol photoreforming is essential.

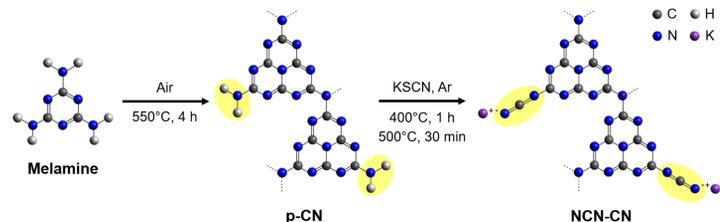


## Aims

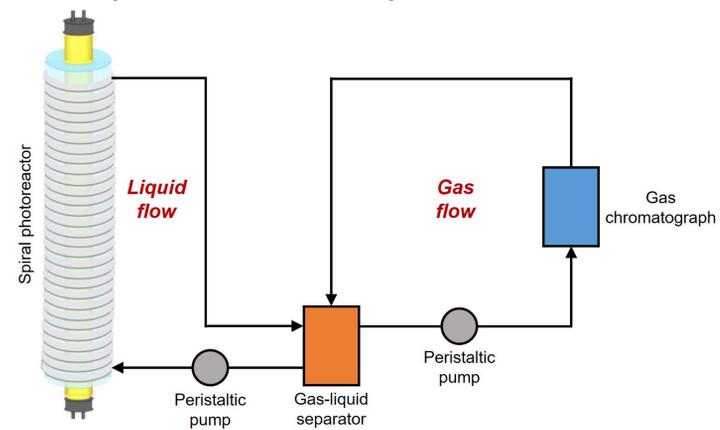
- To engineer *in situ* photodeposited Ni on carbon nitride via cyanamide functionalisation and charge-induced activation for enhanced selective ethanol photoreforming.
- To decouple the synergistic promotional effects by cyanamide groups and excess Ni<sup>2+</sup> in solution.

## Experimental

### Synthesis of Cyanamide-Functionalised Carbon Nitride

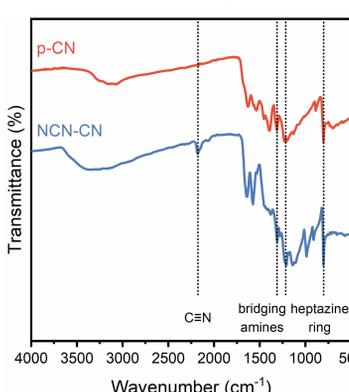


### Online Spiral Photoreactor Setup

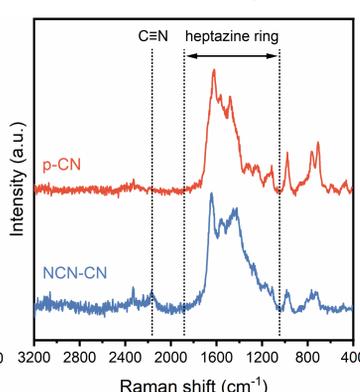


## Identification of Cyanamide Groups

### FTIR Spectroscopy



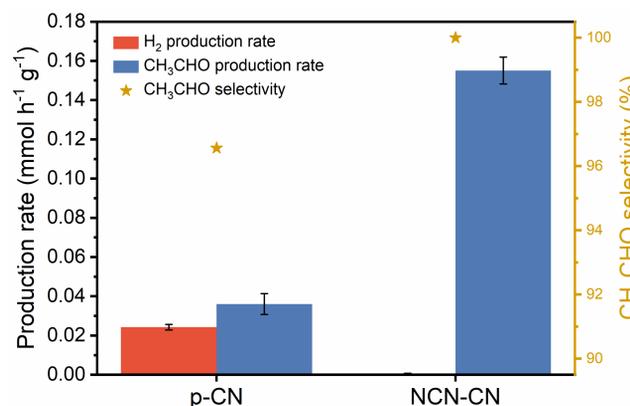
### Raman Spectroscopy



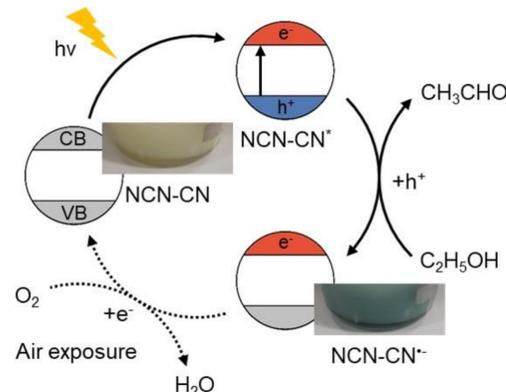
The C≡N stretching IR vibration band and Raman band indicate the presence of cyanamide groups in NCN-CN.

## Role of Cyanamide Groups

### Photoreforming Activity and Selectivity



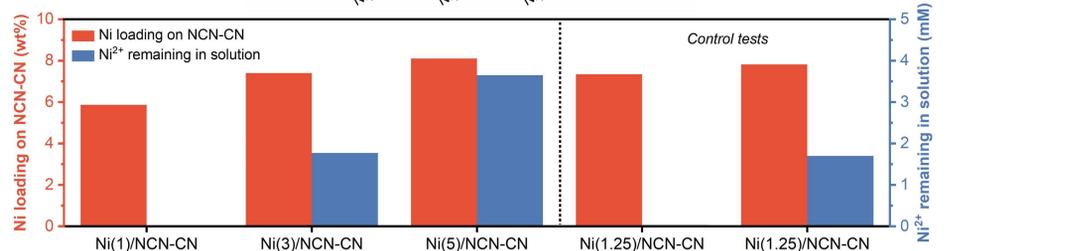
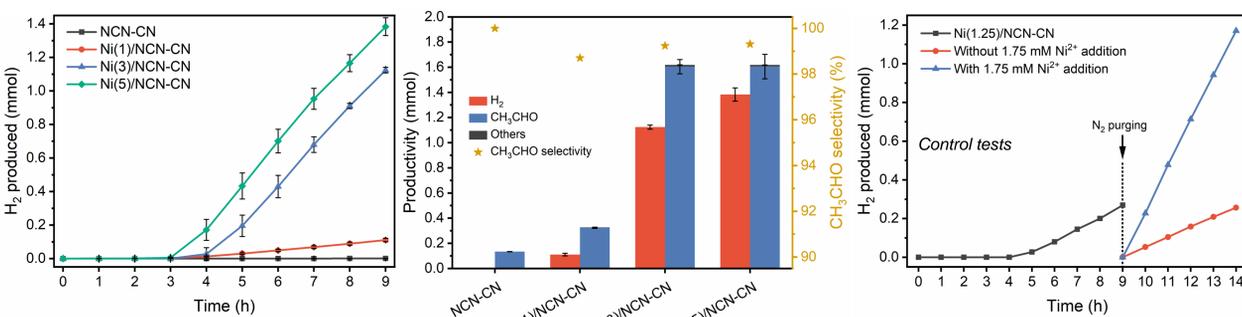
### Redox Photocatalytic Cycle of NCN-CN



Cyanamide groups in NCN-CN induced effective transfer of the photogenerated holes to the ethanol and electron-storing capacity, thus leading to a higher acetaldehyde production but almost no H<sub>2</sub> was detected.

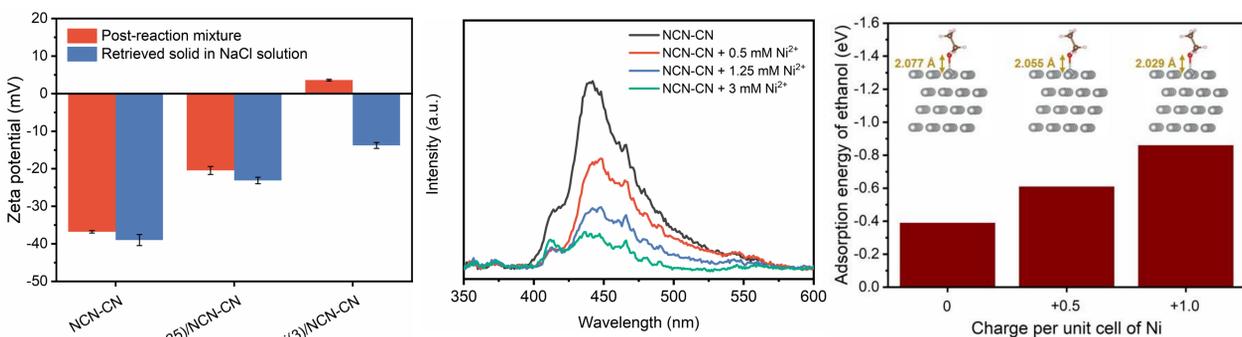
## Role of Excess Ni<sup>2+</sup> in Solution

### Extensive Photoreforming Studies of Ni/NCN-CN and Mass Balance of Ni during the Reaction



Excess Ni<sup>2+</sup> in solution plays a crucial role in enhancing the performance of selective ethanol photoreforming.

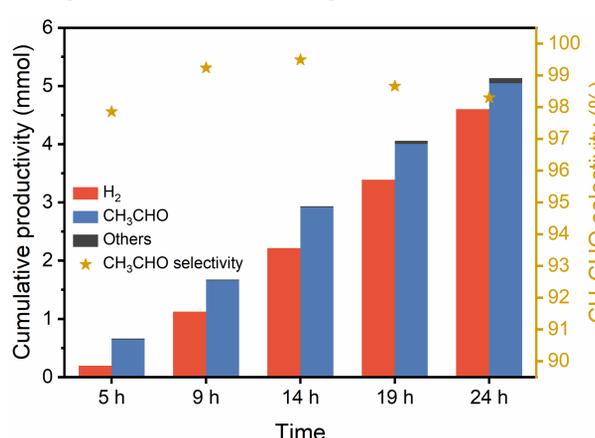
### Elucidating the Contribution of Excess Ni<sup>2+</sup> in Solution during Ethanol Photoreforming



- The presence of excess Ni<sup>2+</sup> created a positively-charged environment on the surface of Ni/NCN-CN.
- As a result, the binding energy of Frenkel excitons in NCN-CN was reduced and ethanol adsorption on Ni active sites was improved.

## Photoreforming Stability

### Long-Term Photoreforming Test of Ni(3)/NCN-CN



## Conclusions

- Synergism between cyanamide functionalisation and *in situ* Ni photodeposition in the presence of excess Ni<sup>2+</sup> invokes an enhanced performance.
- Cyanamide groups promoted hole scavenging for ethanol oxidation reaction, enabling effective electron transfer to Ni for H<sub>2</sub> evolution.
- Excess Ni<sup>2+</sup> ions in solution created a positively-charged environment on the surface, improving charge carrier utilisation and ethanol adsorption.

## References

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- Toe et al., *Energy Environ. Sci.* 2021, **14**(3), 1140-75.
- Uekert et al., *Nat. Sustain.* 2020, **4**, 383-91.
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