

Photocatalytic CO₂ Reduction with Two-Dimensional Conductive Metal-Organic Frameworks



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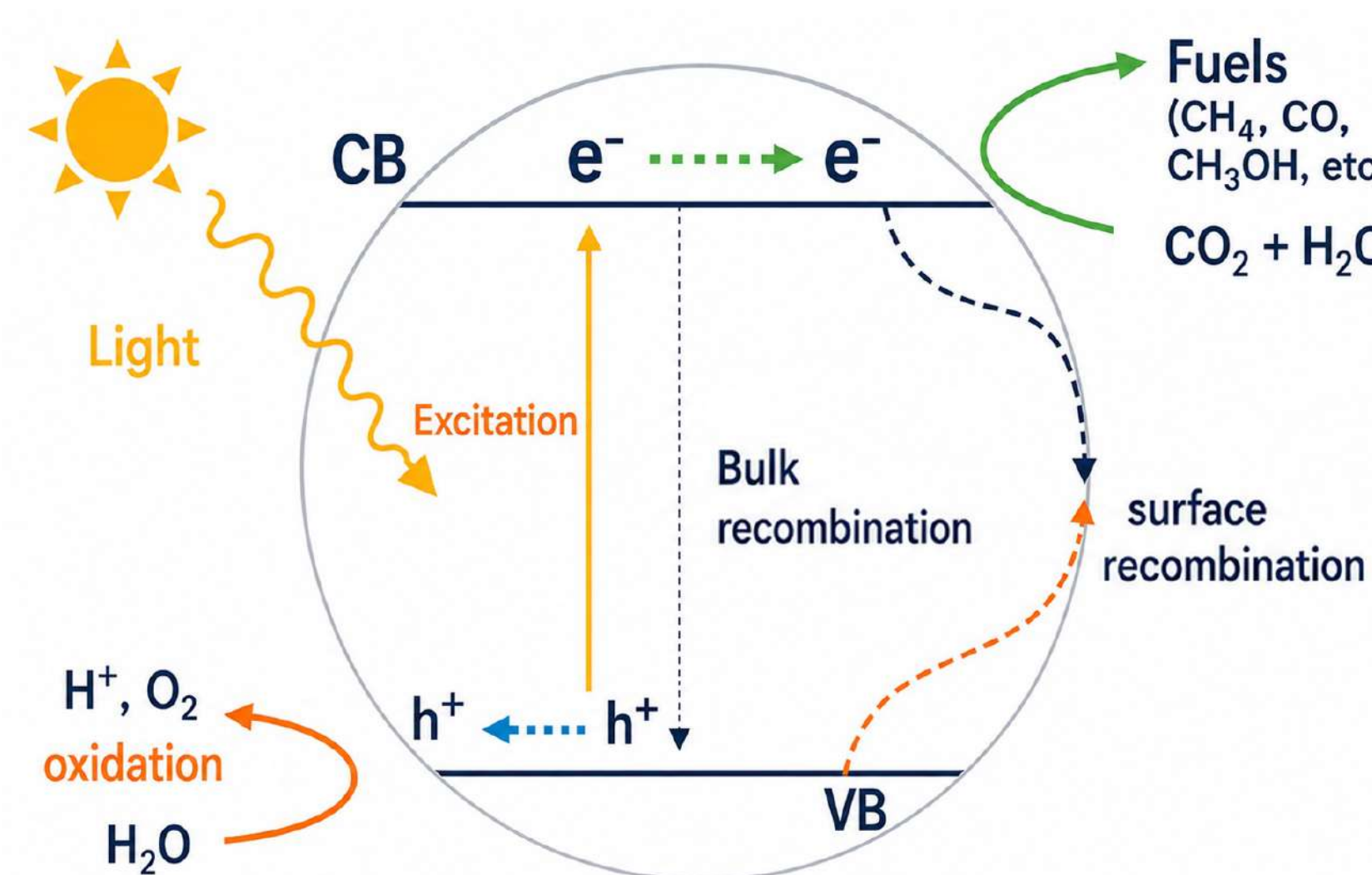
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Abstract

Photocatalytic CO₂ reduction has attracted significant attention as a promising approach for converting greenhouse gases into value-added fuels using solar energy. In this study, HHTP-based metal-organic frameworks (M-HHTP, M = Fe, Ni, Co, and Cu) were successfully synthesized and coupled with carbon nitride (CN) to construct heterostructure photocatalysts for CO₂ reduction. The incorporation of CN enhanced interfacial charge transfer and improved the photocatalytic activity of the M-HHTP materials. Among all the synthesized samples, FeHHTP/CN exhibited the highest CO evolution performance, which was attributed to its suitable band positions and balanced charge-transfer characteristics. This work demonstrates a feasible strategy for constructing conductive MOF/CN heterostructures for efficient photocatalytic CO₂ reduction.

Introduction



Industrialization has steadily increased atmospheric CO₂ concentrations. Photocatalytic CO₂ reduction is a promising strategy for converting CO₂ into valuable fuels using solar energy. However, its application remains limited due to its low photocatalytic efficiency.

Experimental Procedures

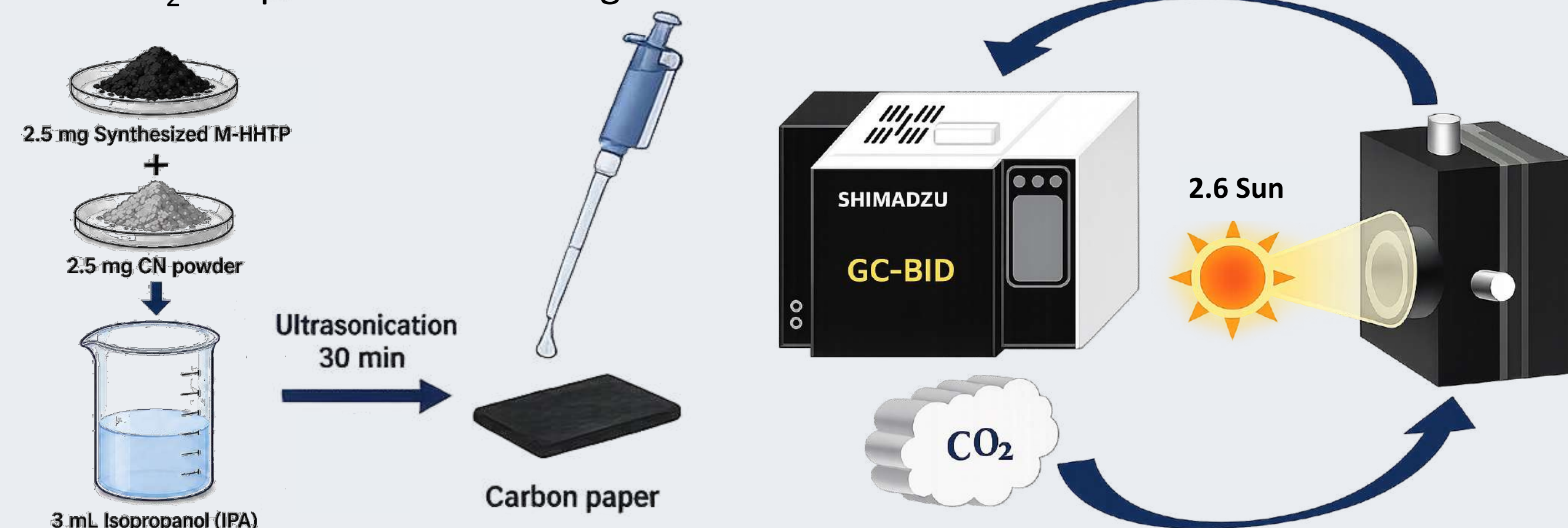
I. Synthesis process

- Schematic illustration of M-HHTP formation

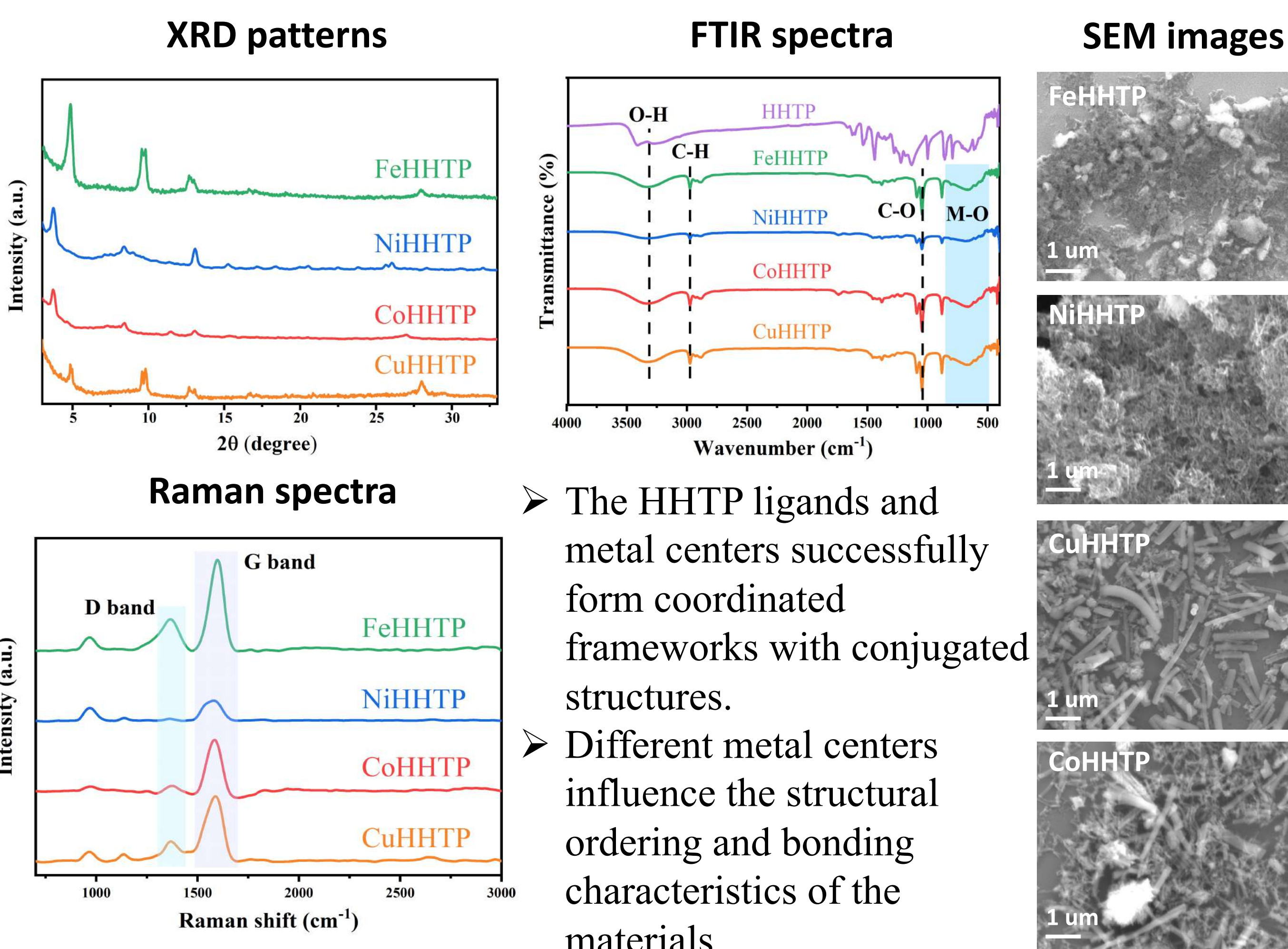


II. Photocatalytic Carbon Dioxide Reduction Reactions

- Photocatalytic measurement was conducted by gas-phase CO₂ reduction with H₂O vapor under 2.6 Sunlight irradiation.

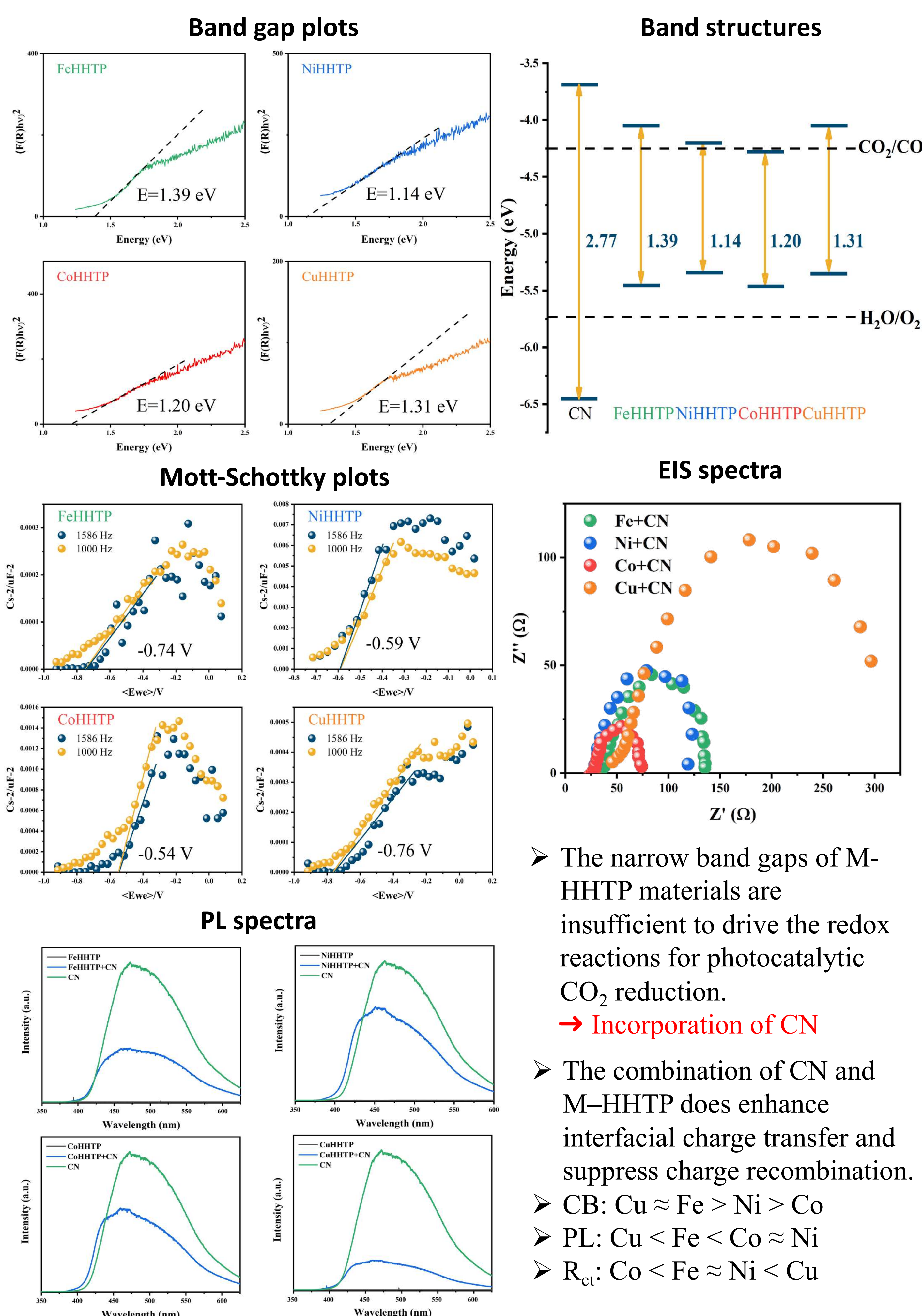


Material Characterizations



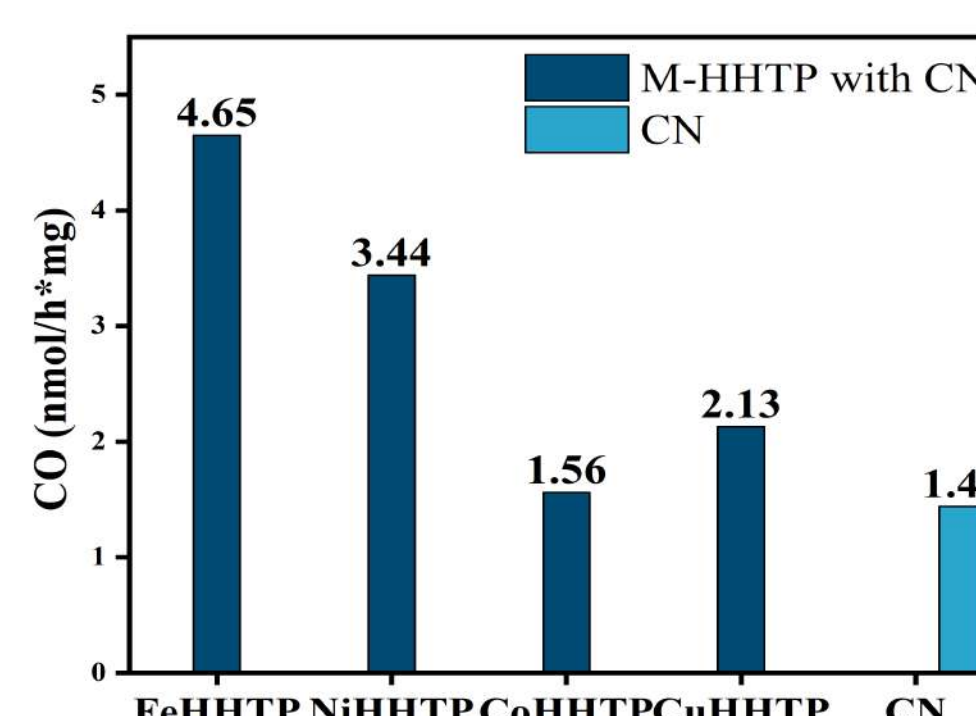
- The HHTP ligands and metal centers successfully form coordinated frameworks with conjugated structures.
- Different metal centers influence the structural ordering and bonding characteristics of the materials.

Heterostructure Analysis



- The narrow band gaps of M-HHTP materials are insufficient to drive the redox reactions for photocatalytic CO₂ reduction.
➔ **Incorporation of CN**
- The combination of CN and M-HHTP does enhance interfacial charge transfer and suppress charge recombination.
- CB: Cu ≈ Fe > Ni > Co
- PL: Cu < Fe < Co ≈ Ni
- R_{ct}: Co < Fe ≈ Ni < Cu

Photocatalytic CO₂ Reduction Reactions



- Carbon oxide (CO) was detected as the main product.
- The combination of M-HHTP and CN enhances the photocatalytic CO₂ reduction performance.
- FeHHTP with CN exhibits the highest CO evolution rate.

Conclusion

We successfully synthesized HHTP-based metal-organic frameworks for photocatalytic CO₂ reduction. The incorporation of CN enhances charge transfer and photocatalytic activity of the M-HHTP materials. Among all samples, FeHHTP with CN exhibited the highest CO evolution performance, which can be attributed to its suitable band positions and the balanced charge-transfer characteristics. This work demonstrates a strategy for constructing conductive MOF with CN heterostructures toward efficient photocatalytic CO₂ reduction.

Acknowledgment

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