



Regulating the Metal Sites of Prussian Blue Analogues Photocatalysts for Carbon Dioxide Reduction Reactions



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Abstract

Photocatalytic CO₂ reduction driven by solar energy is a promising sustainable strategy to address climate change. This study investigates the material design and reaction behavior of Prussian Blue Analogues (PBAs) in CO₂ photoreduction by synthesizing a series of PBA photocatalysts with varied M-site metal compositions. Among all samples, Ni-PBA achieves the highest CO yield, demonstrating that M-site identity governs charge transfer and product selectivity. The findings serve as a reference for the rational design of low-cost CO₂ photocatalysts.

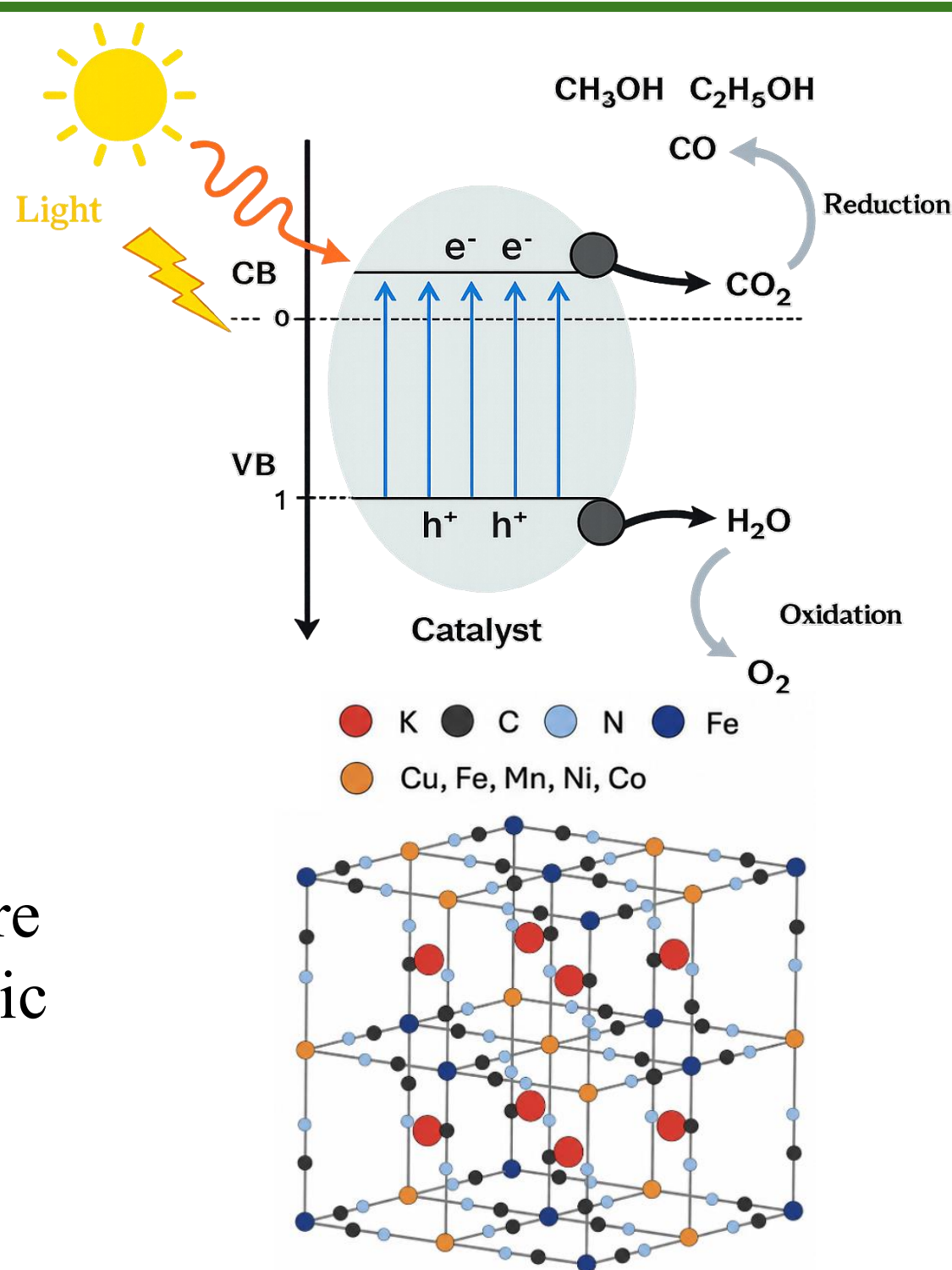
Photocatalytic CO₂RR

Mechanism in 3 steps

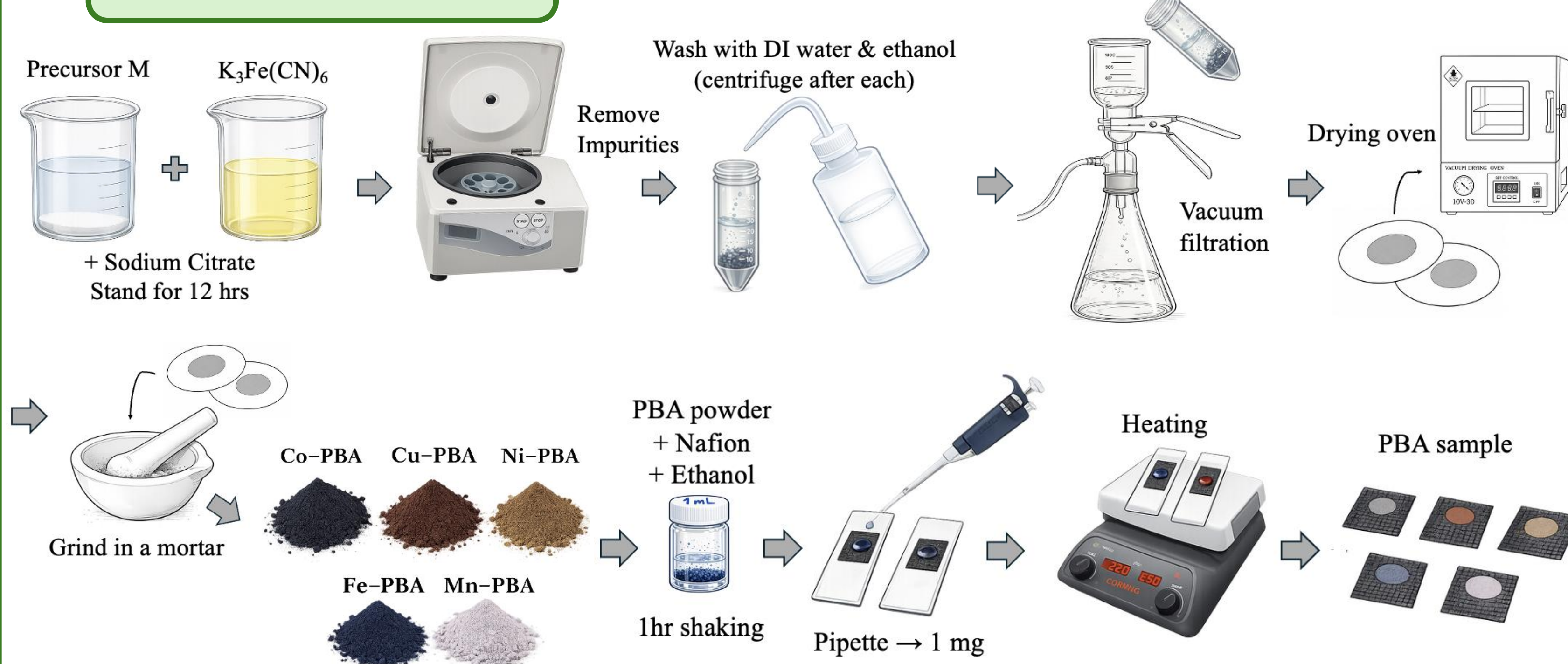
- (1) light absorption → e⁻ and h⁺
- (2) e⁻ reduces CO₂ / h⁺ drives oxidation
- (3) products form at the catalyst surface

PBAs Structure

PBAs adopt a cubic framework with M-N≡C-Fe-C≡N-M connectivity, where tunable M-site metals modulate electronic structure and catalytic behavior.

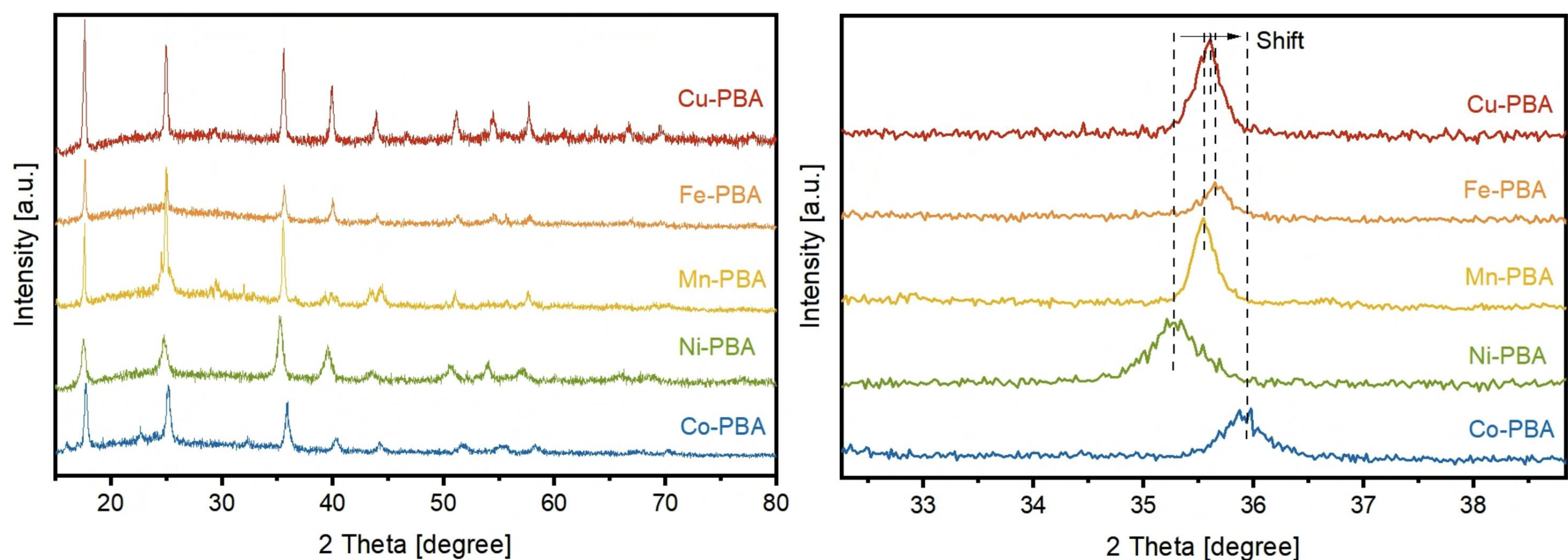


Experiment process

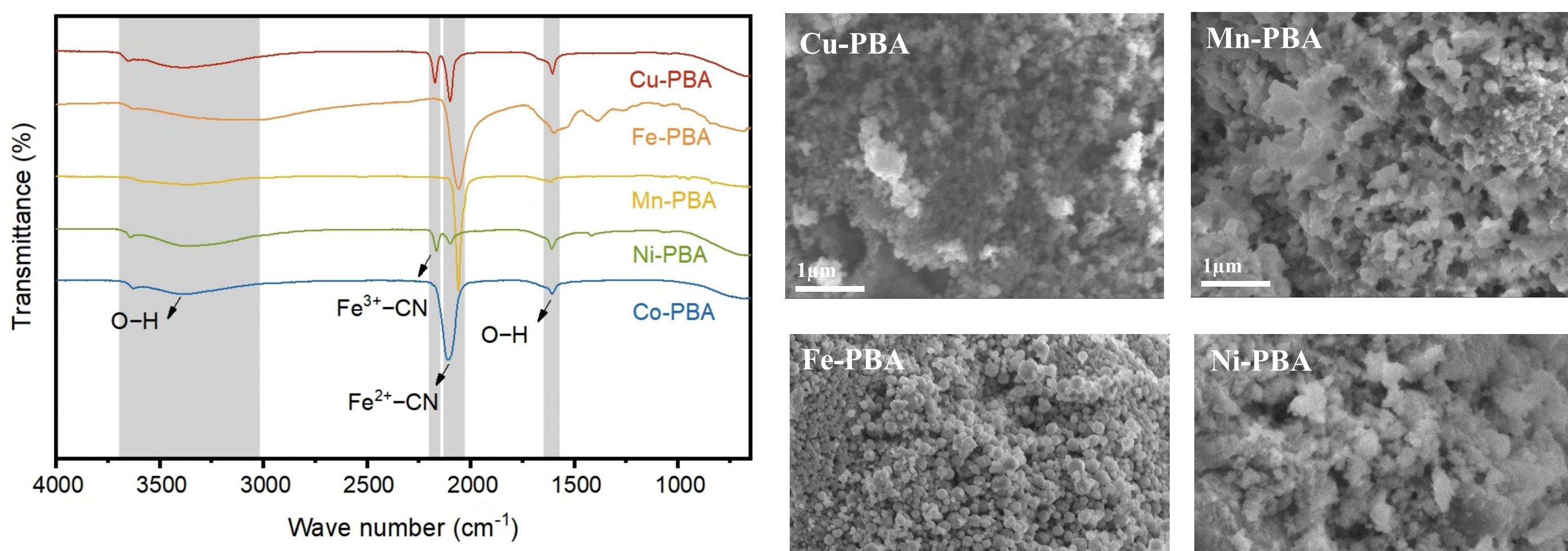


Results & Discussion

Material Analysis



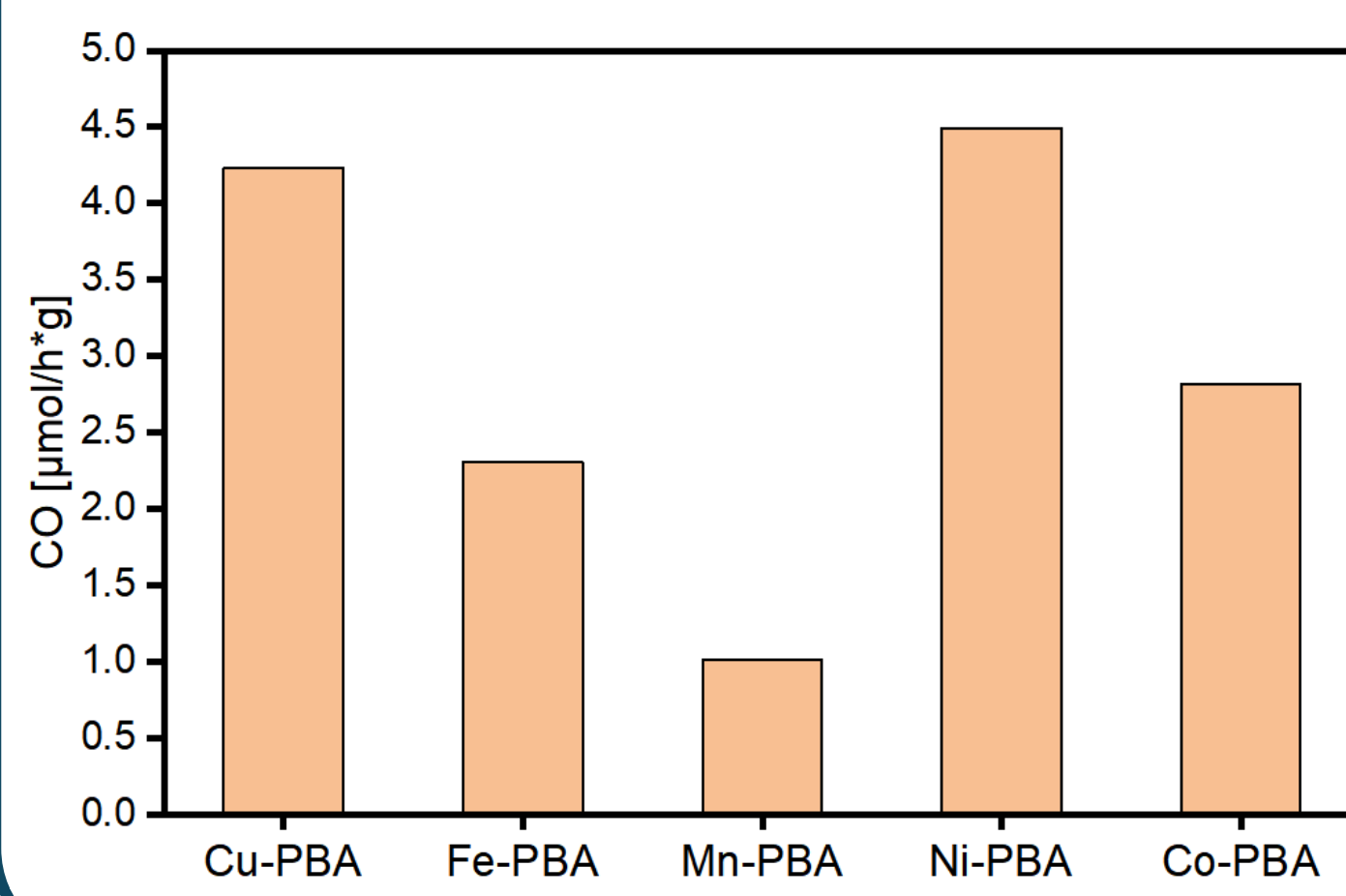
- XRD confirms the cubic F43m PBA structure for all M-PBA samples, with peak positions shifting across different M-site metals, reflecting changes in lattice constants due to varying ionic radii.



- FT-IR reveals both Fe³⁺-CN (2160 cm⁻¹) and Fe²⁺-CN (2080 cm⁻¹) stretching vibrations, indicating mixed-valence Fe at the M' site.

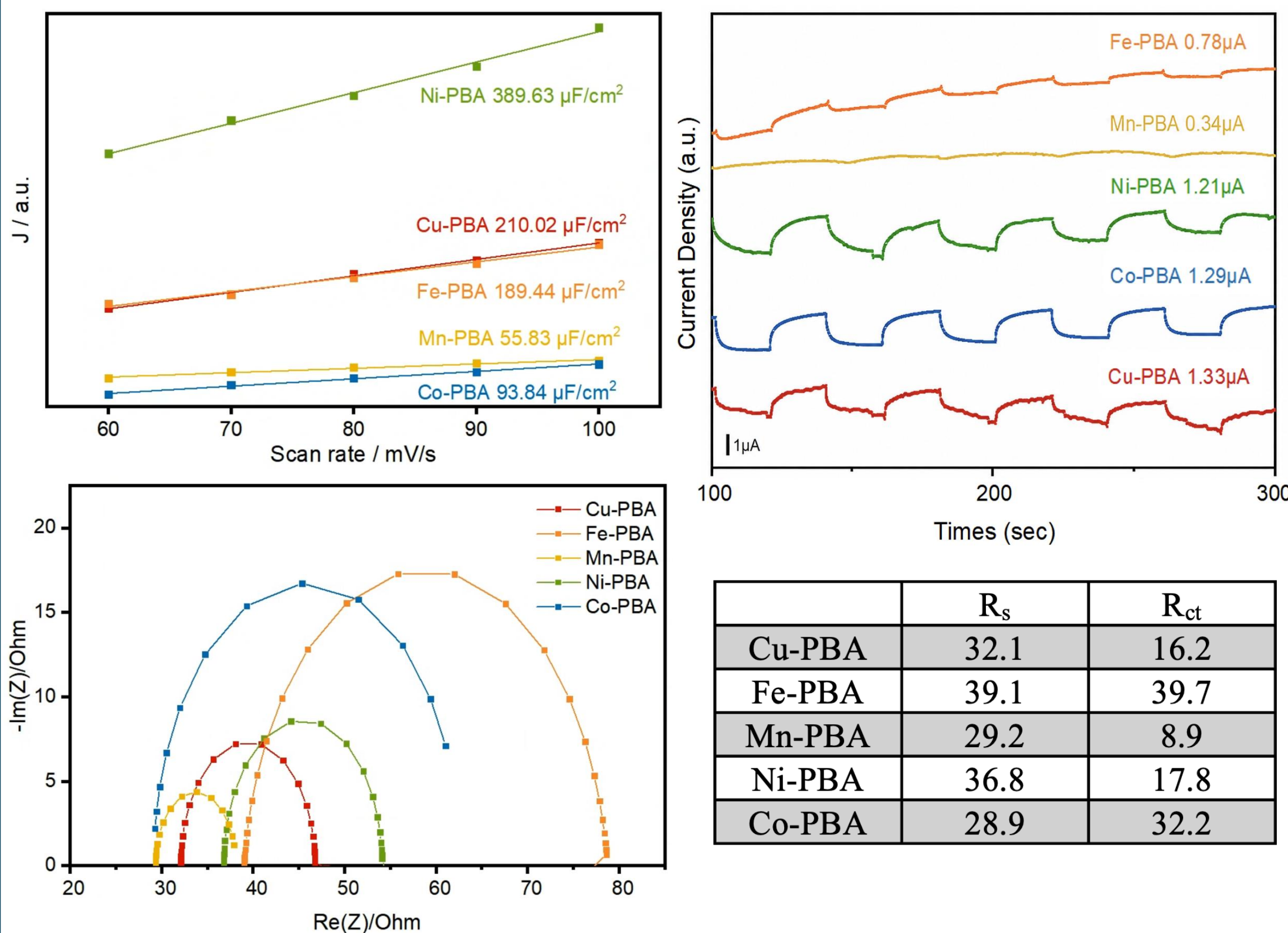
- SEM confirms nanoscale morphology and homogeneous distribution across all M-site PBA samples.

Photocatalytic CO₂ Reduction



- Ni-PBA and Cu-PBA exhibit the highest CO production rates among all M-site PBA samples.
- Samples exhibiting Fe³⁺-CN stretching vibrations in FT-IR correlate with superior CO yields, suggesting that the presence of Fe³⁺ at the M' site facilitates charge transfer and activates CO₂ reduction sites.

Electrochemical Measurements



- Neither ECSA nor R_{ct} alone governs performance, their synergy determines photoelectrochemical activity.

- Ni-PBA shows the highest ECSA, indicating the most accessible active sites

- Cu-PBA exhibits the highest photocurrent, reflecting superior charge generation and separation efficiency.

- Mn-PBA shows the lowest R_{ct}, while Fe-PBA shows the highest, revealing M-site metal-dependent charge transfer kinetics.

Conclusion

- (1) All M-PBA samples were successfully synthesized via co-precipitation, confirmed to adopt the cubic F43m structure by XRD.
- (2) FT-IR reveals mixed-valence Fe³⁺/Fe²⁺ at the M' site, a higher Fe³⁺/Fe²⁺ ratio correlates with superior CO yields in Ni-PBA and Cu-PBA.
- (3) Electrochemical results are consistent with catalytic performance: Ni-PBA's highest ECSA and Cu-PBA's highest photocurrent both support their superior CO yields, while Fe-PBA's highest R_{ct} and Mn-PBA's lowest ECSA limit their activity.
- (4) M-site metal identity governs both charge transfer kinetics and CO₂RR selectivity, providing a reference for rational PBA catalyst design.

Reference

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Acknowledgment

MOE-UAAT-CFC-11401, MOE-110-YSFEE-0005-002-P1, NSTC 114-2221-E-006 -136 -MY4, NSTC 114-2923-E-006-004, NSTC 113-2628-E-006-001, Higher Education Sprout Project of the Ministry of Education to the Headquarters of University Advancement at National Cheng Kung University