European Polymer Federation (EPF 2025), Martiniplaza, Groningen, the Netherlands

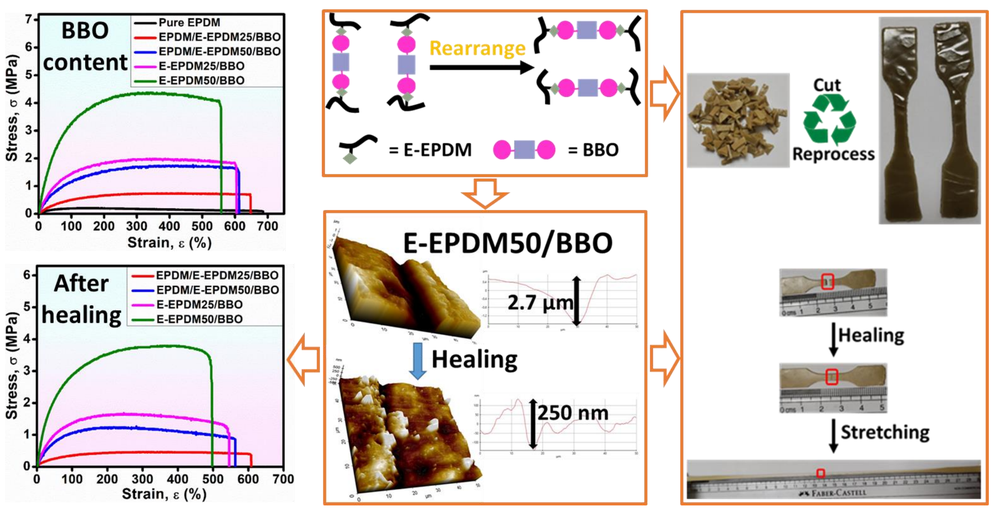
Dual Dynamic Cross-linking in EPDM Elastomer

Atif Ansari, *Bhavya Parameswaran, Nikhil Kumar Singha**

Rubber Technology Centre, Indian Institute of Technology, Kharagpur

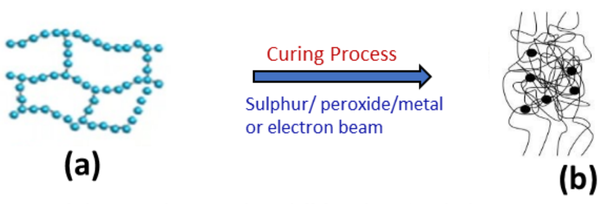
**Corresponding author:* nks8888@yahoo.com

Abstract: Covalently cross-linked elastomers are widely recognised for their excellent elasticity, which makes them essential for a number of applications such as medical implants, tires, seals etc. It is extremely desired to develop flexible and self-healing rubbers since they are capable of being reprocessed to increase their lifespan and reduce environmental pollution. This work demonstrates a straightforward approach to develop mechanically resilient, healable, and recyclable elastomeric vitrimer based on EPDM elastomer. This was accomplished by using a dynamic dual cross-linker, which can induce disulphide metathesis as well as transesterification reaction in epoxidized EPDM. In this case, the EPDM was epoxidised to prepare E-EPDM by using meta-chloroperoxybenzoic acid (mCPBA) as an epoxidising agent. The epoxidation of EPDM is confirmed by ^{1}H NMR and FT-IR analyses. The dynamic dual cross-linker with disulphide linkage bearing dicarboxylic groups, i.e., (4,4'-((disulfanediylbis(4,1-phenylene))bis(azanediyl))bis[4-oxobutanoic acid] (BBO)) was synthesized by reacting of 4-aminophenyl disulphide and succinic anhydride in DMF solvent at ambient temperature under inert atmosphere. The formation of cross-linker was confirmed by ^{1}H NMR, MALDI-TOF, and FT-IR analyses. The epoxy group of E-EPDM reacted with dicarboxylic groups in BBO to form β-hydroxy ester functional groups, which undergo exchange reaction. This exchange reaction along with the metathesis reaction of disulphide present in BBO installs mechanical resilience, self-healing, and reprocessibility in the modified EPDM.

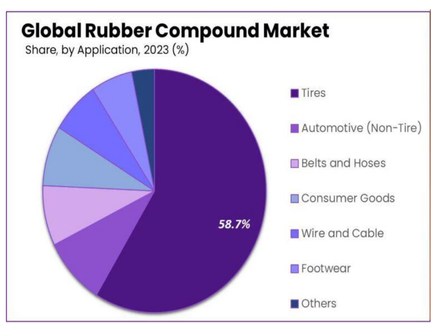


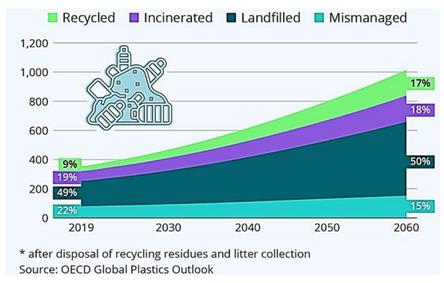
INTRODUCTION

Why vulcanization is required ?

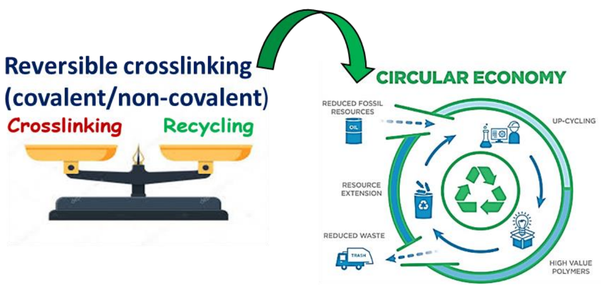


(a) Un-vulcanized and **(b)** vulcanized elastomers





Solution



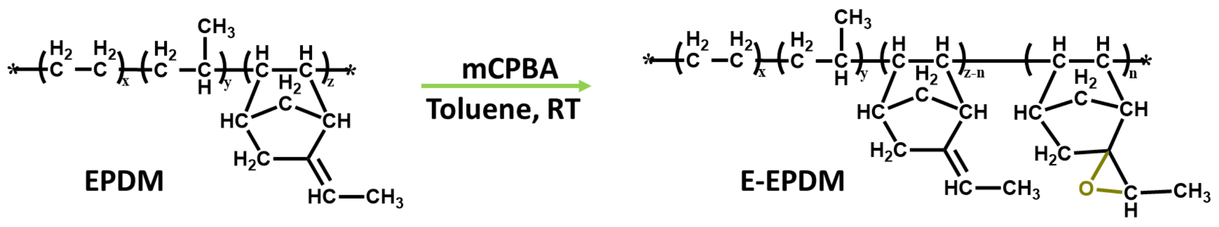
METHODS

Preparation of disulphide linkage and β-hydroxy ester functional groups rich composite based on epoxy functionalized EPDM (E-EPDM)

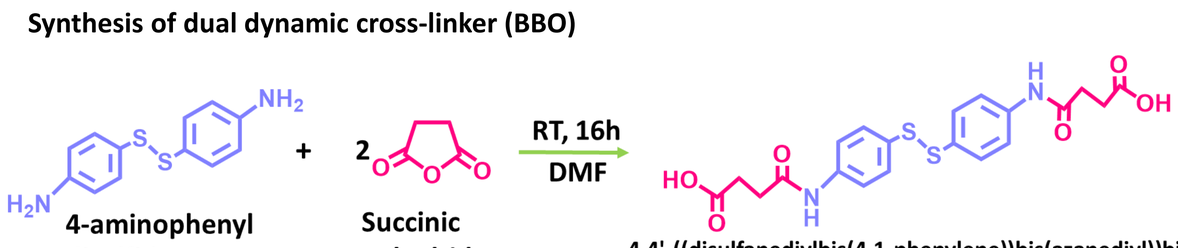
Study the self-healing characteristics as well as dynamic and mechanical properties

Epoxydation of EPDM → **Synthesis of dynamic dual cross-linker** → **Mixing of E-EPDM and cross-linker** → **Moulding at 160 ℃ under 15 MPa**

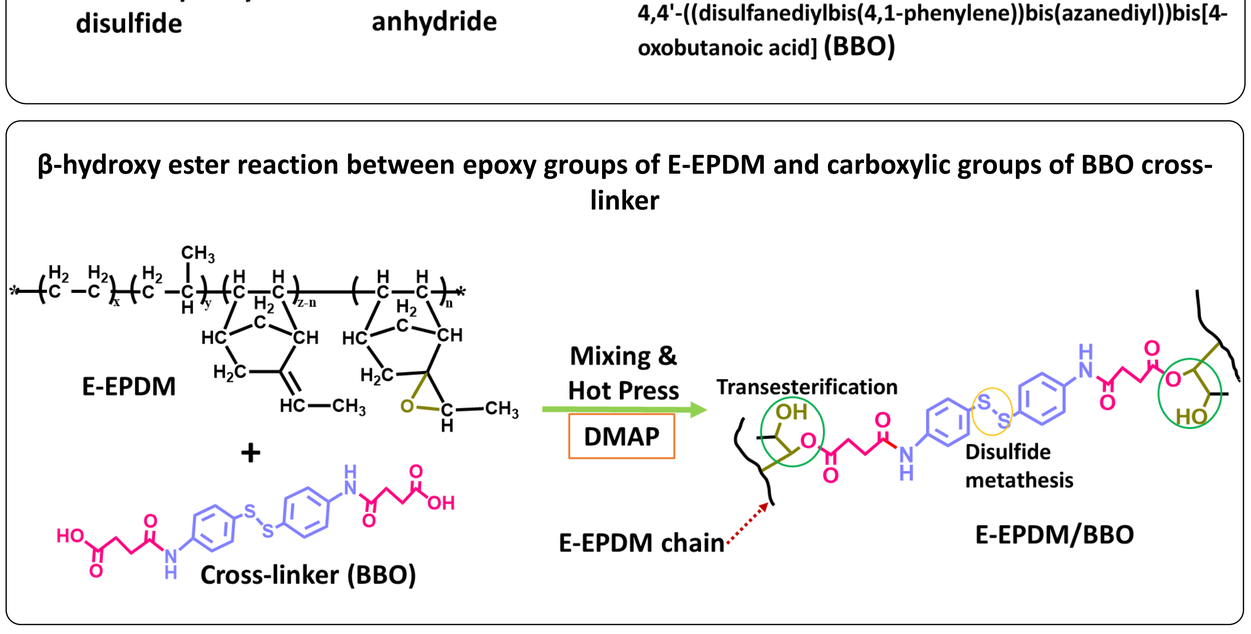
Epoxidation of EPDM



Synthesis of dual dynamic cross-linker (BBO)

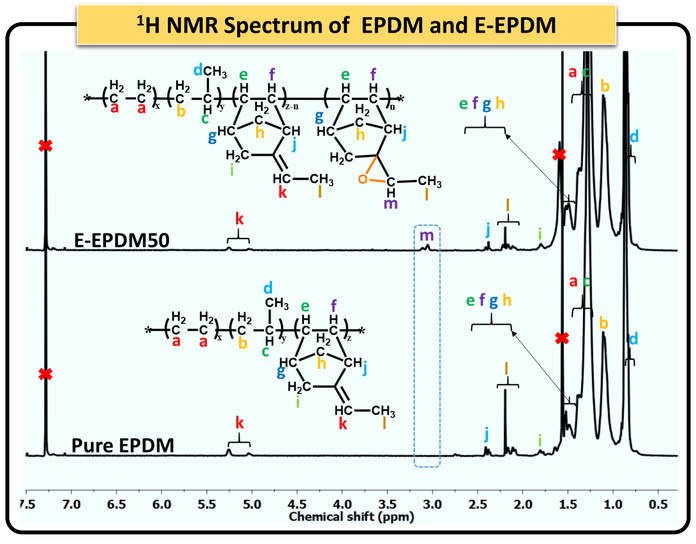


β-hydroxy ester reaction between epoxy groups of E-EPDM and carboxylic groups of BBO cross-linker

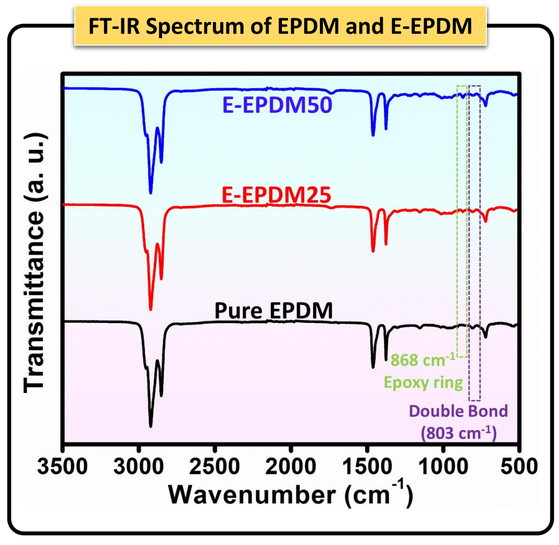


RESULTS

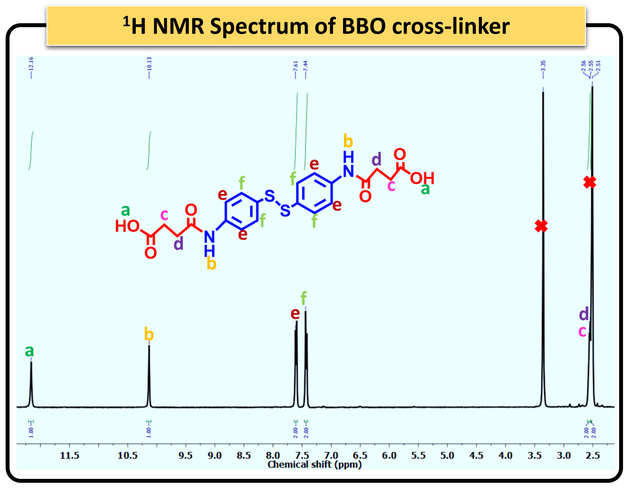
^{1}H NMR Spectrum of EPDM and E-EPDM



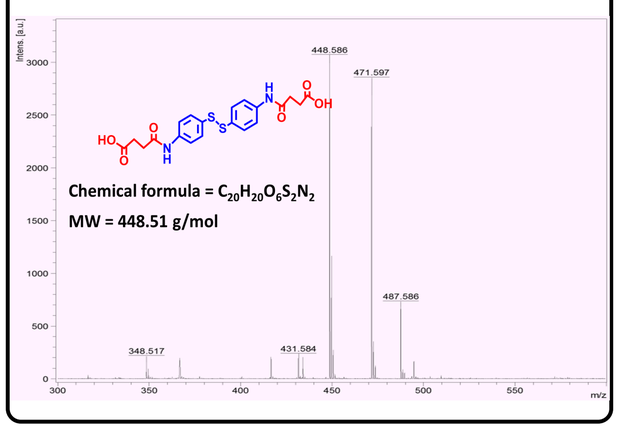
FT-IR Spectrum of EPDM and E-EPDM



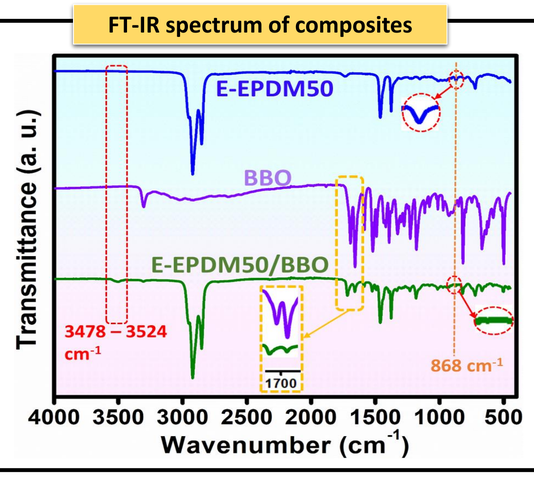
^{1}H NMR Spectrum of BBO cross-linker



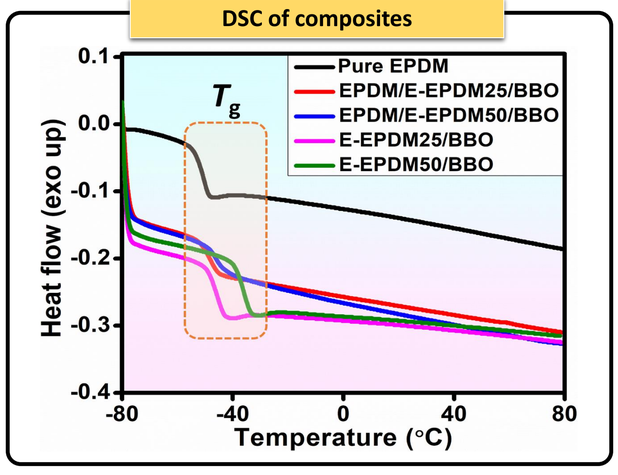
MALDI-TOF of BBO cross-linker



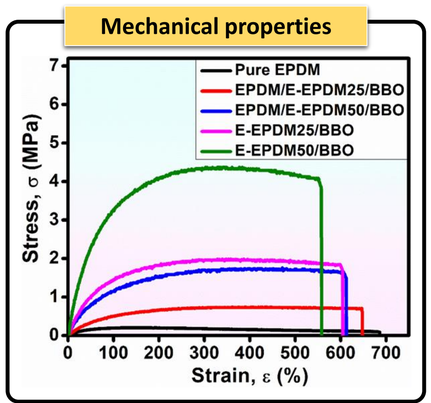
FT-IR spectrum of composites



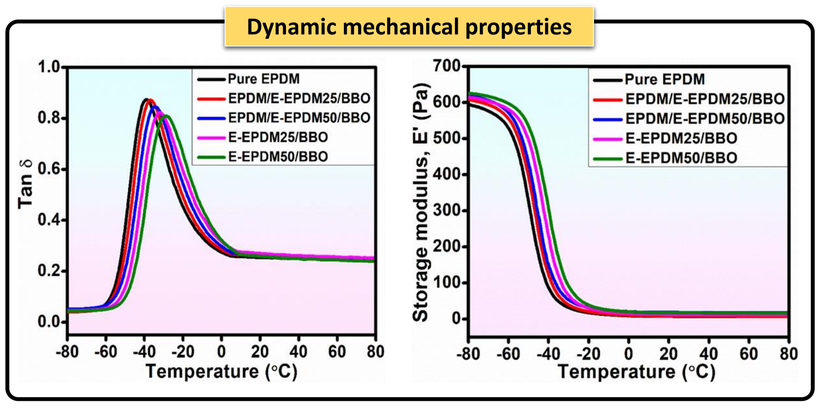
DSC of composites



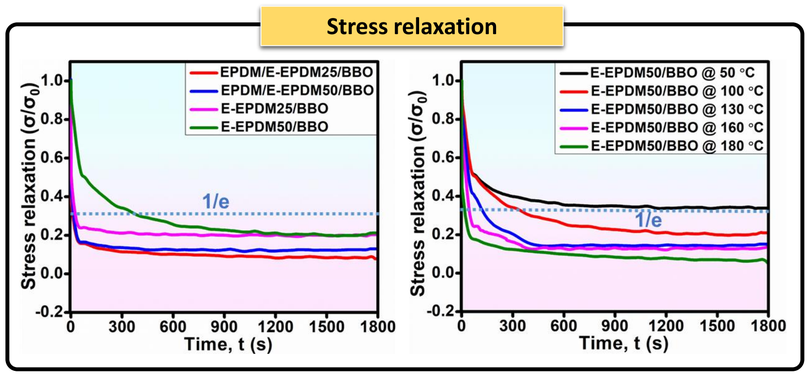
Mechanical properties



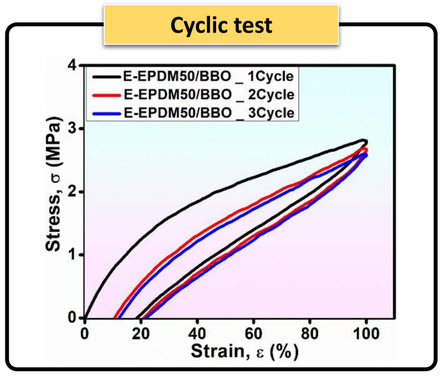
Dynamic mechanical properties



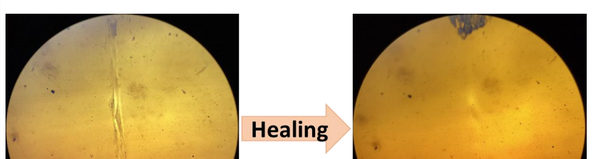
Stress relaxation



Cyclic test

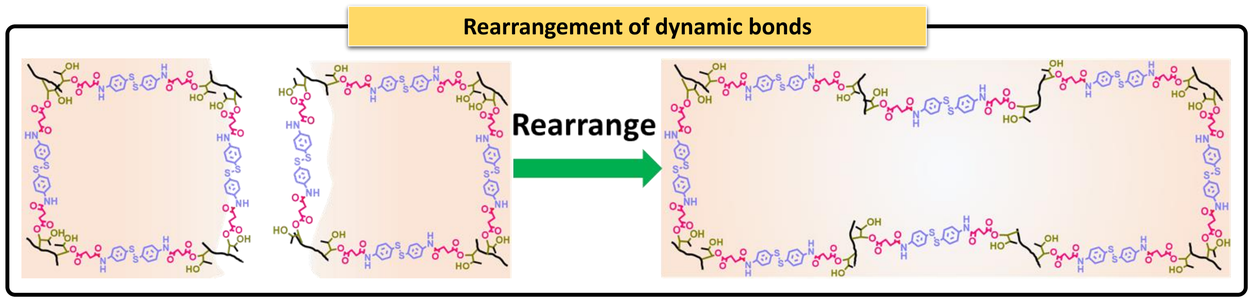


Optical microscopy

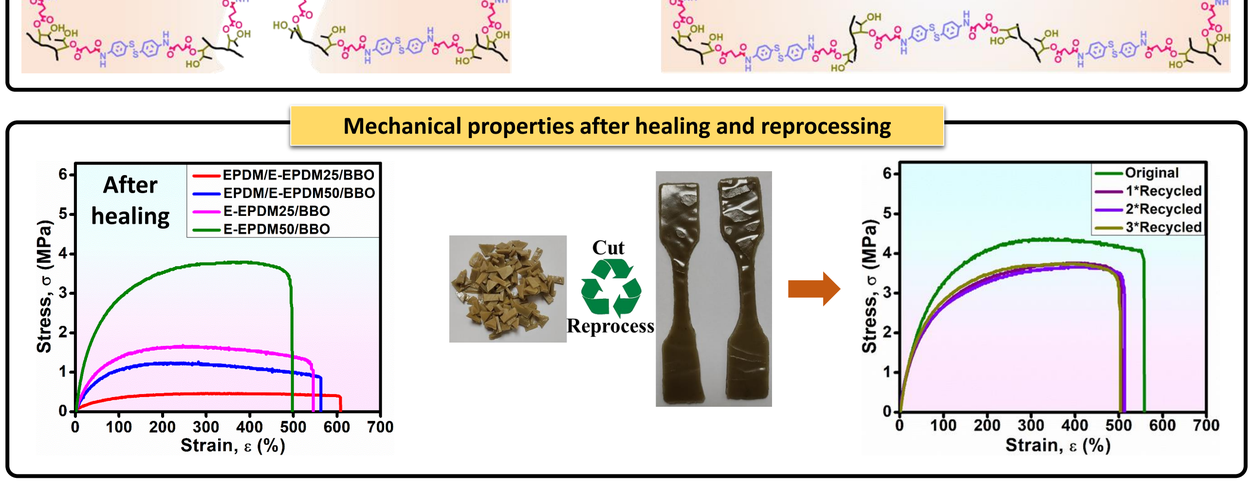


AFM

Rearrangement of dynamic bonds



Mechanical properties after healing and reprocessing



CONCLUSION

- This work deliver a straightforward approach based on widely available diene rubber to generate permanently cross-linked, self-healing, and recyclable elastomers by incorporating a dynamic, reversible transesterification and disulfide conjunction into the network.
- The variation in cross-linker amount can effectively alter the mechanical characteristics of the composites that were obtained.
- The E-EPDM networks associated with covalent bonds have the potential to modify their topology dynamically via the interchange of disulfide and β-hydroxy ester, whereby they might be self-healed, recycled, and reshaped.

REFERENCES

[1] Chen, Y.; Tang, Z.; Liu, Y.; Wu, S.; Guo, B. Mechanically Robust, Self-Healable, and Reprocessable Elastomers Enabled by Dynamic Dual Cross-Links. Macromolecules 2019, 52 (10), 3805–3812. https://doi.org/10.1021/acs.macromol.9b00419.

[2] Parameswaran, B.; Sarkar, S.; Badhra, S.; Nair, S.; Singha, N. K. Designing Self-Healing in Styrene–Butadiene Rubber via Polysulfide Crossover Reactions. ACS Appl. Eng. Mater. 2024. https://doi.org/10.1021/acsaenm.4c00314.

ACKNOWLEDGEMENT

Authors acknowledge Indian Institute of Technology Kharagpur for the infrastructural support. Atif Ansari thanks MHRD for the fellowship