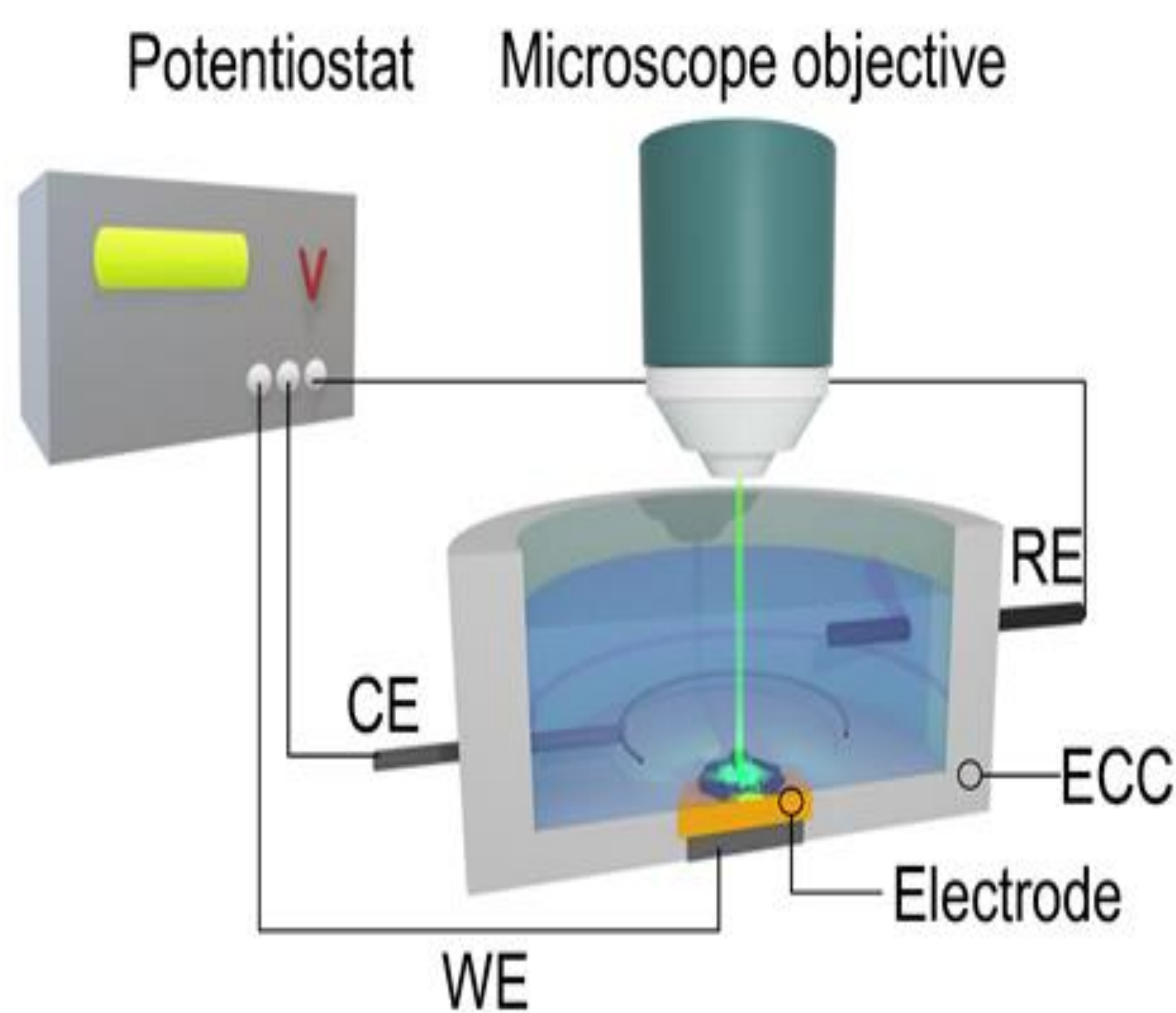
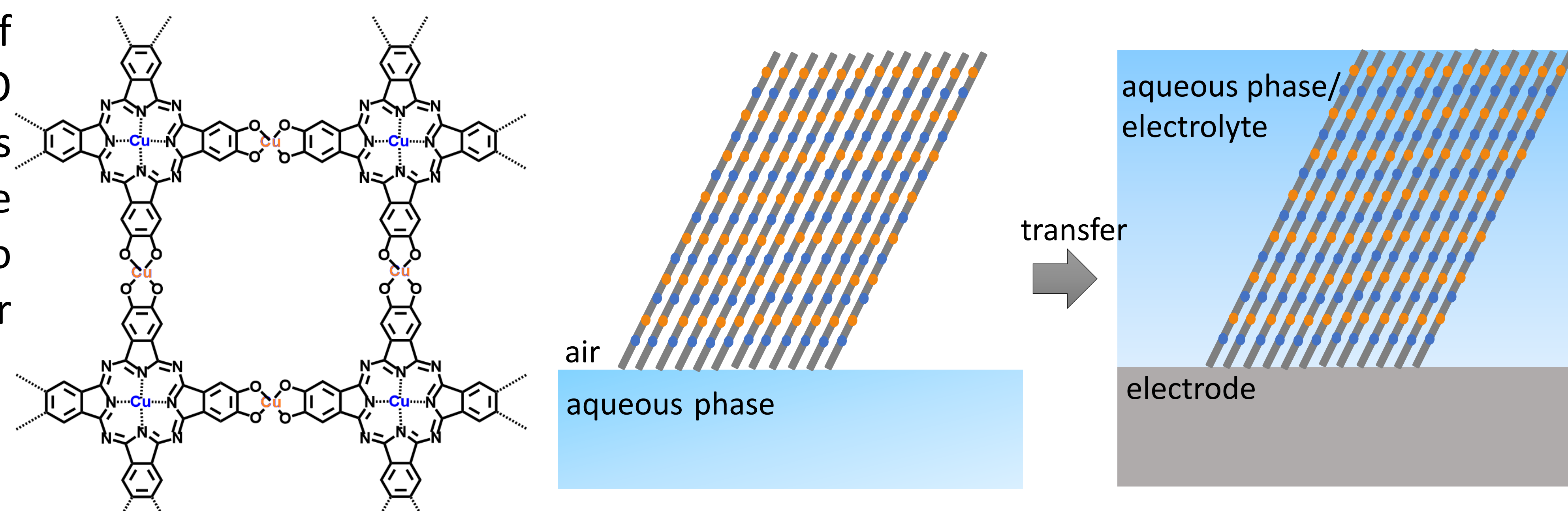


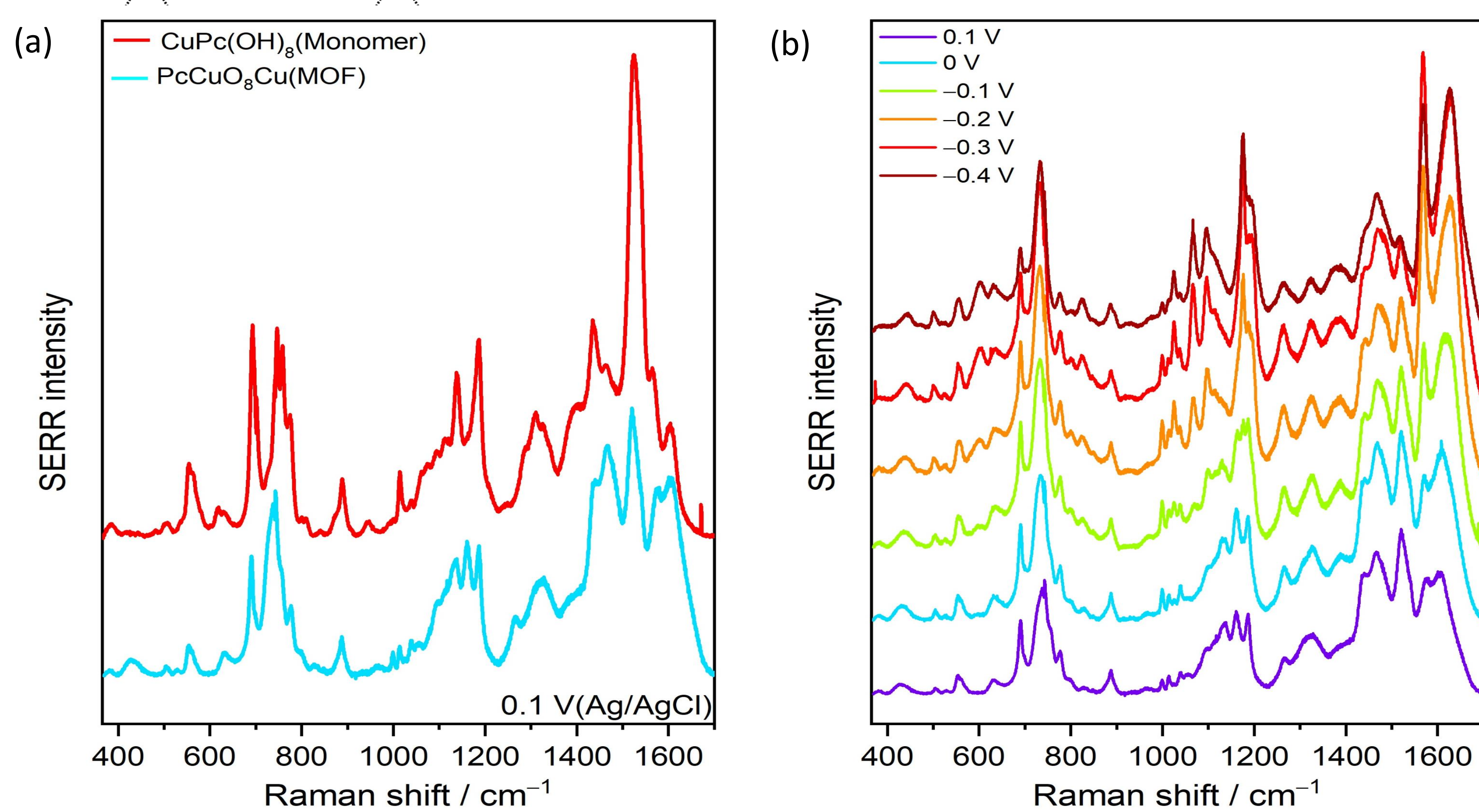
Mechanistic Insights into the redox properties of conjugated 2D-MOFs via electrochemical Raman Spectroscopy

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Metal Organic Frameworks (MOFs) consisting of Phthalocyanine monomers (Pc) linked by Cu-O were synthesized on a water air interface, and is arranged perpendicular to the surface. The CuPc-CuO₄ MOFs were subsequently attached to roughened silver electrodes through Langmuir Blodgett technique.



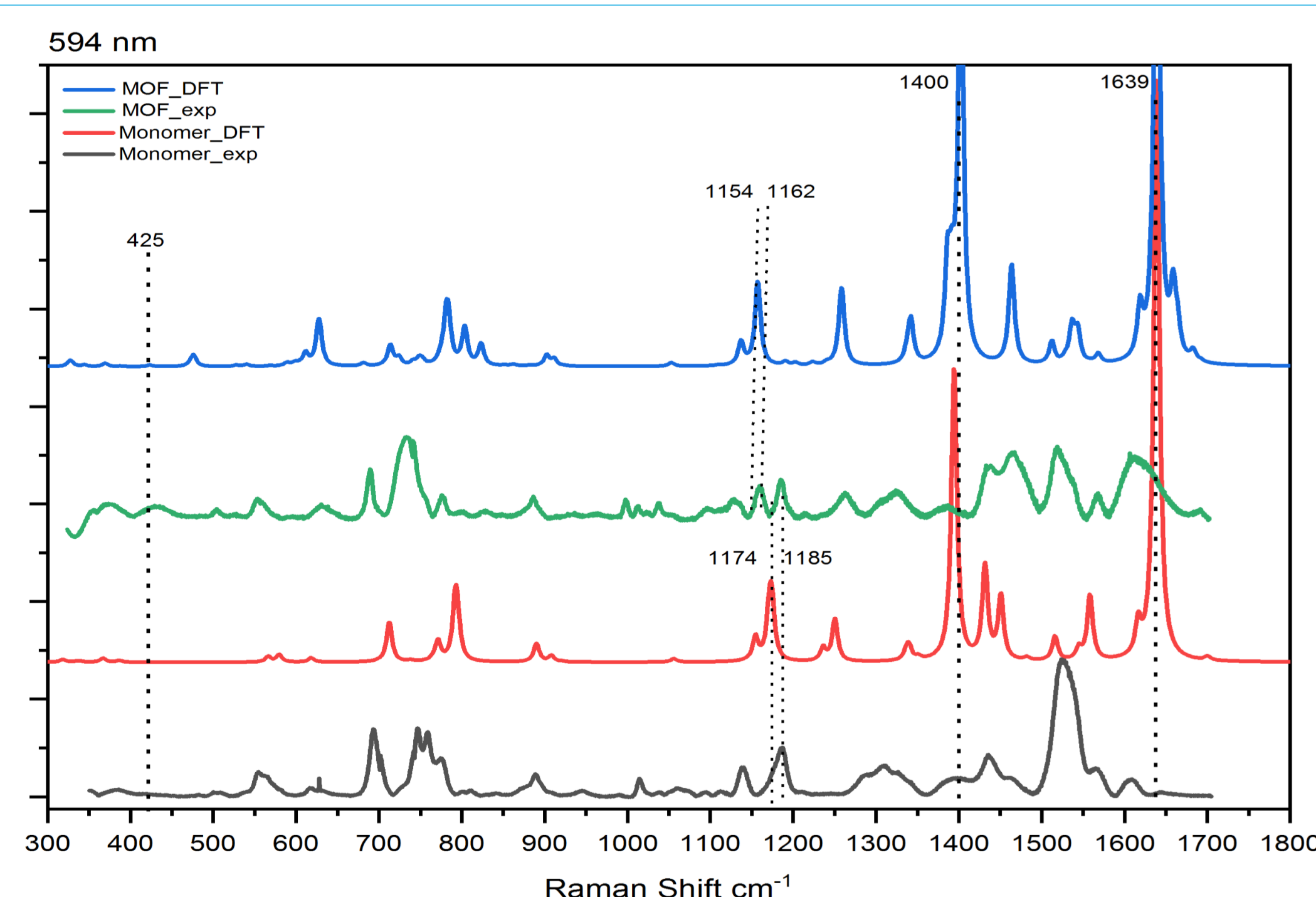
Electrochemical-Raman in the confocal mode carried out in standard electrochemical cells (ECC) Exciting laser light focussed via the microscope objective on the sample-deposited WE (Working electrode) Electrical potentials are applied using a potentiostat. CE (Counter Electrode), RE (Reference Electrode)



Surface enhanced Resonance Raman Spectrum of (a) PcCu(OH)₈ and CuPcCuO₄ for comparison and (b) CuPcCuO₄ with varied potential

Raman spectra of MOF and monomer were measured while applying potentials to the electrode to understand the redox changes happening while reduction. Both the Monomer and MOF regains all the signals on reoxidising it back to a positive potential, proving that they are an irreversible system. Although, the spectra of MOF and monomer looks almost identical, there are unique peaks which are present in both of them, which gives us important information on the redox potentials of Phthalocyanine in the monomer, MOF and Cu in the O-nodes

DFT Simulations were done on both monomer and MOF which helped in visualisation of the vibration corresponding to each peak. Vibrations were mainly classified as two: the ones localized on the oxygen nodes and the ones localized on the Phthalocyanine unit. The band at 425, which is absent in monomer, represents a vibration of the O-H bond. The band seen at 1154 in the MOF is seen to be shifted to 1174 in the monomer and they both represent vibrations involving oxygen, thereby participates actively in polymerization. Prominent peaks at 1400 and 1600 representing Phthalocyanine vibrations undergo significant changes in intensities as they are reduced



Conclusion: With the help of DFT simulations and *In-situ* Raman experiments we have been able to assign most Raman peaks to determine the redox properties of the MOF. Further efforts needs to be done to properly attach the MOF in graphite electrodes and study the electrochemical oxygen reduction reaction.

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