# 2D-GRAPHENE SHIELDED GOLD METASURFACE FOR ENHANCED GREEN HYDROGEN EVOLUTION REACTION BY PHOTOELECTROCHEMICAL WATER SPLITTING

Muhammad Haris[1,2], Klaudijus Midveris[1,2], Syeda Ammara Shabbir[3,4], Carlos Ponce de Leon[3,4], Mohamed Ahmed Baba[2], Gvidas Klyvis[2], Algirdas Lazauskas[2], Erika Rajackaitė[2], Mindaugas Andrulevičius[2], Mindaugas Juodėnas[2], Asta Tamulevičienė[1,2], Tomas Tamulevičius[1,2], Sigitas Tamulevičius[1,2]

[1]Kaunas University of Technology, Department of Physics, Lithuania Studentų St. 50, LT, 51368, Kaunas, Lithuania
[2]Kaunas University of Technology, Institute of Materials Science, K. Baršausko St. 59, LT, 51423, Kaunas, Lithuania
[3]Forman Christian College, Department of Physics, Lahore, Pakistan
[4]University of Southampton, Faculty of Engineering and Physical Sciences, Southampton, SO17 1BJ, UK
muhhar@ktu.lt

This study presents a novel design of a graphene-capsulated gold plasmonic ordered nanoparticle (NP) array on conductive oxide as a photoelectrode for enhanced hydrogen evolution reaction (HER) via photoelectrochemical (PEC) water splitting. The 100 nm diameter and 400 nm pitch Au NP array self-assembled in the template and transferred on the fluorine tin oxide-coated glass substrate (FTO) substrate exhibited a shift from conventional surface lattice resonance to a hybrid plasmonic wave-guided mode at 631 nm wavelength .The microwave-enhanced chemical vapour deposition grown of a single atomic layer graphene film acted as a protective barrier for Au NPs, stabilized Fermi level pinning, and improved the junction from Schottky to ohmic, enabling faster charge transfer through thermionic and quantum tunneling effects. The photoelectrode with Au NP metasurface on FTO substrate with graphene film as a shielding barrier on top (FTO/Au(Metasurface)/G1L) achieved superior HER performance with an onset potential of −0.55 V(Ag/AgCl) and a photocurrent of −0.36 mA/cm2 under visible light. A maximum photocurrent of −6.2 mA/cm2 obtained under visible-light excitation confirms that HER solely originated from photoinduced excitation. This high activity resulted from rapid interband transitions in Au NPs, which generated hot carriers and promoted efficient charge mobility. Graphene semi encapsulation retained and protected Au NPs and their intrinsic plasmonic attributes in an electrochemical environment while enhancing photocatalytic kinetics. Overall, PEC tests confirmed that this tailored electrode minimized charge recombination, ensured steady current under bias, and delivered excellent solar-to-hydrogen performance with 0.35% applied bias photon-to-current efficiency, 70% external quantum efficiency, and nearly 100% internal quantum efficiency. This makes the FTO/Au(Metasurface)/G1L a promising photocathode for efficient and stable green hydrogen production.

**Acknowledgements**
This project has received funding from the Research Council of Lithuania (LMTLT), agreement no S-MIP-23-93

**Keywords:** Gold nanoparticles array, Surface lattice resonance, Capillarity-assisted particle assembly, Hybrid waveguided plasmonic mode, Graphene, Fermi level pinning, Helmholtz layer, Hydrogen evolution reaction, Thermionic emission, Thermionic field emission,