Single-step strategy for the development of hybrid GaON/ZnO/FTO Photoanodes for enhanced water oxidation

Ibrahim Khan, Ahsanulhaq Qurashi

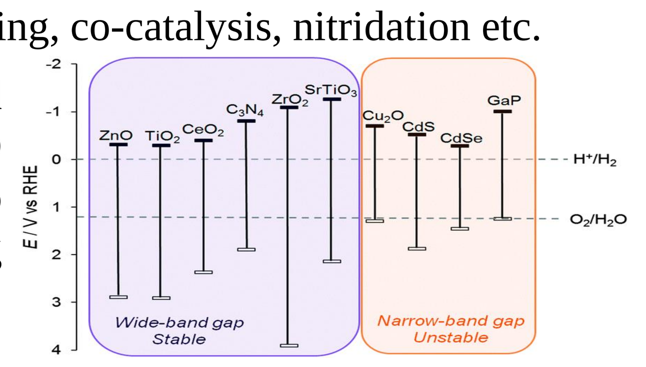
Abstract

Synthesis of GaON/ZnO hybrid nanoarrays (NAs) was achieved by single step pulse sonicated wet Chemistry. The intercalation of GaON nanosheets through ZnO nanotubes revealed by FE-SEM technique, while elemental analysis is carried out by EDX and X-ray Photoelectron Spectroscopy (XPS) profiling. EDX confirmed Ga, O, Zn and N elements, while XPS established the Ga-N, Ga-O and other bond formations. XRD and Raman shifts give significant evidence of GaON/ZnO hybrid formation. The optical properties of GaON/ZnO NAs evaluated via UV-Visible/DRS, and Photoluminescence (PL) spectroscopies. Chemical nitridation and intercalation of GaON in ZnO, caused upward shift of valence band and band gap reduction with delayed photoexcitons recombination. Water splitting via oxidation under 1 SUN irradiation shown significant photocurrent density of 1.2 mA/cm^2 for GaON/ZnO NAs, with higher stability as compared to pristine ZnO and GaON. The Electron Impedance Spectroscopy (EIS), further suggested the ease of charge transfer in the GaON and ZnO interface as we got minimum impedance value for the hybrid.

Introduction

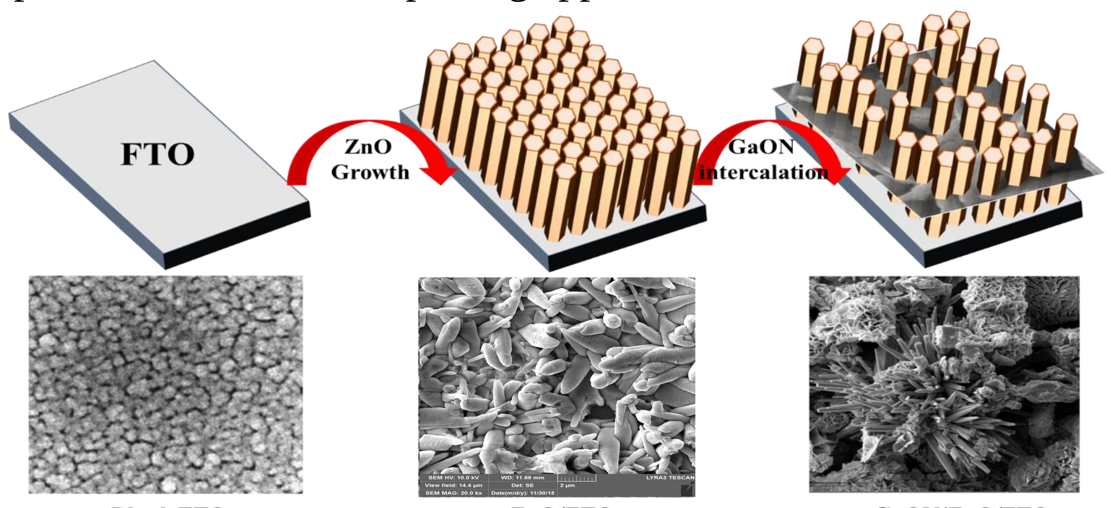
Environmental issues (CO_2 emission) and clean energy at a global level are presently most important concerns raised recently in COP21 in Paris. It is indispensable to construct clean energy systems in order to solve energy related issues and protect our environment. Hydrogen will play an important role in the system because it is an ultimate clean energy source [1]. Hydrogen has tremendous prospective as a fuel and energy source, but the technology needed to realize that potential is still in the early stages. Thus, the design of efficient artificial photosynthesis systems for harvesting solar energy by production of molecular O_2 and H_2 from water splitting has become one of the foremost challenges in the development of a solar driven oxygen and hydrogen generation [2]. Different wide and narrow bandgap materials have been employed. The bandgap of these photoactive materials can be tuned by various techniques, including composite formation, doping, co-catalysis, nitridation etc.

Herein we synthesized nitrogen rich GaON/ZnO hybrid photoanodes to study their water splitting performance.



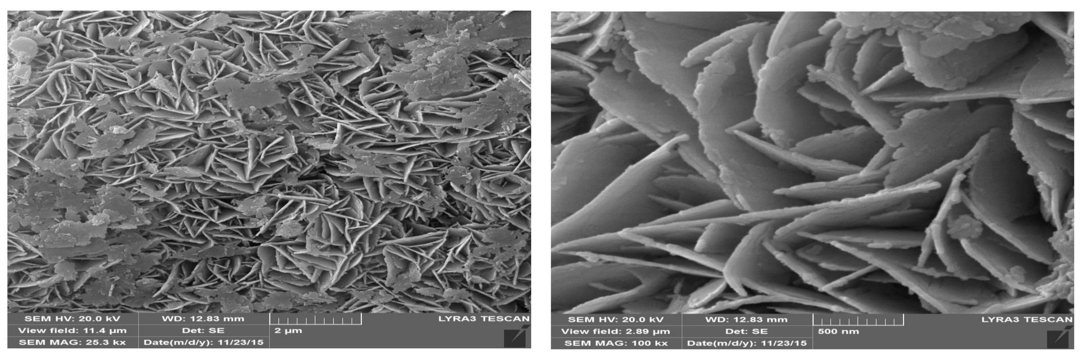
Methodology & Growth Mechanism

ZnO nanotubes were grow on FTO substrate via solvothermal technique. The as prepared GaON nanosheets were intercalate within ZnO nanotubes via pulse sonication technique. The GaON/ZnO hybrid NAs were used as photoanode for water splitting applications.

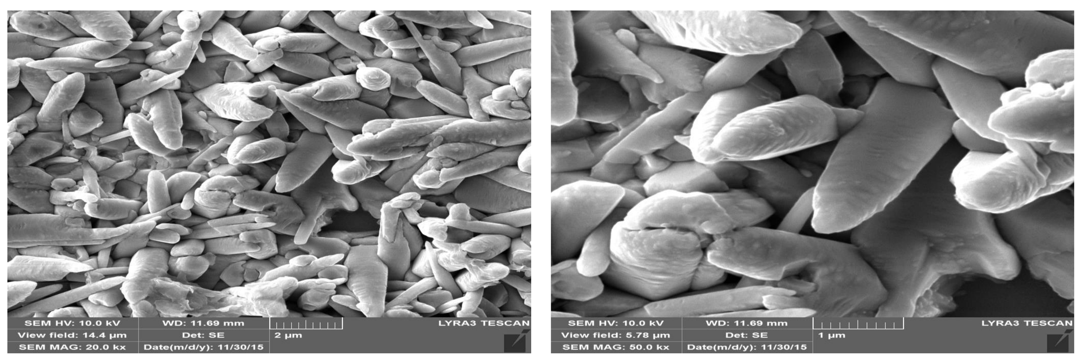


Solar Simulator and Electrochemical Work Station

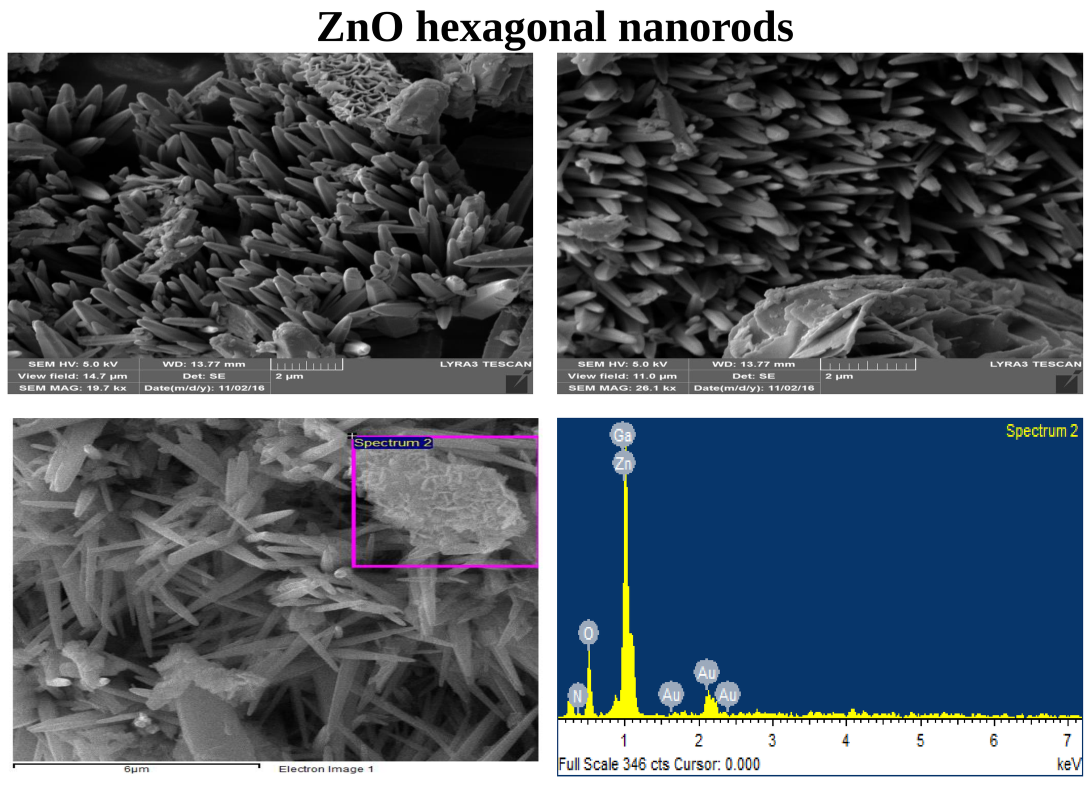
Morphological Study



GaON nanosheets



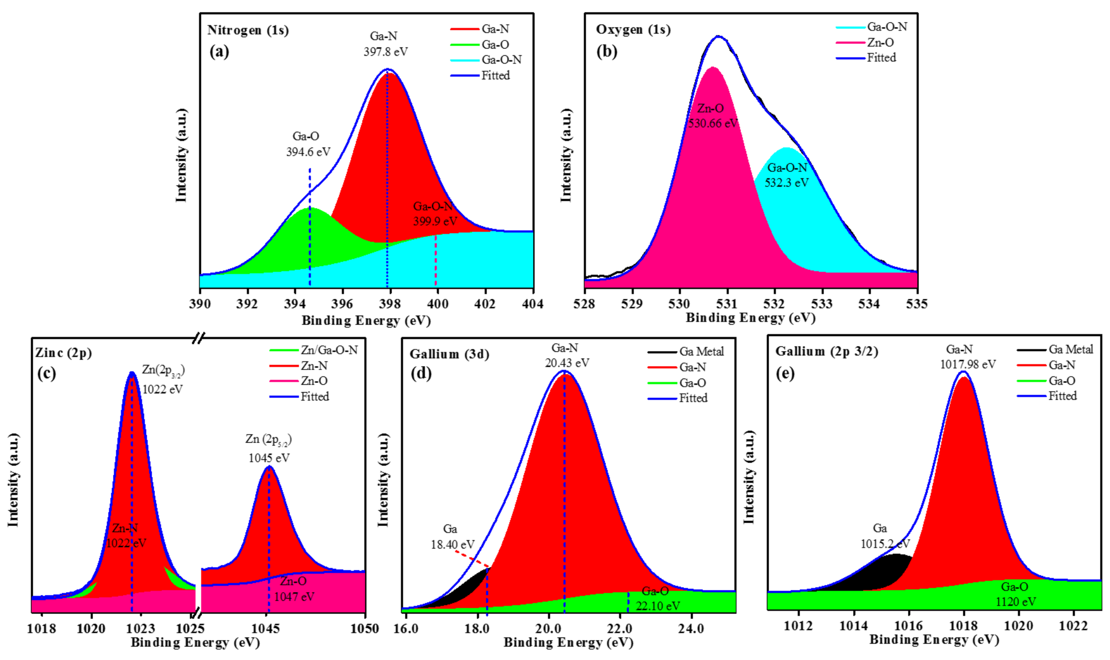
ZnO hexagonal nanorods



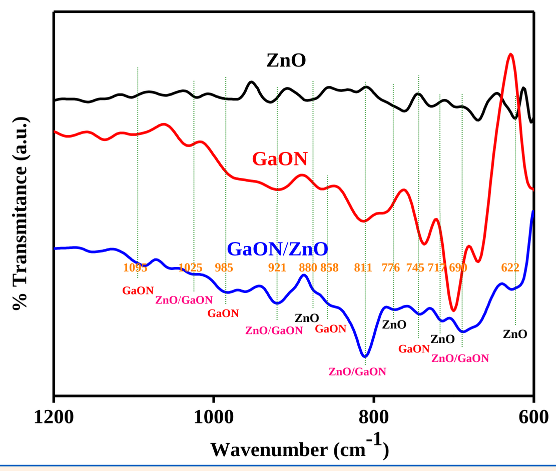
GaON/ZnO hybrid nanoarrays

Structural Properties of GaON

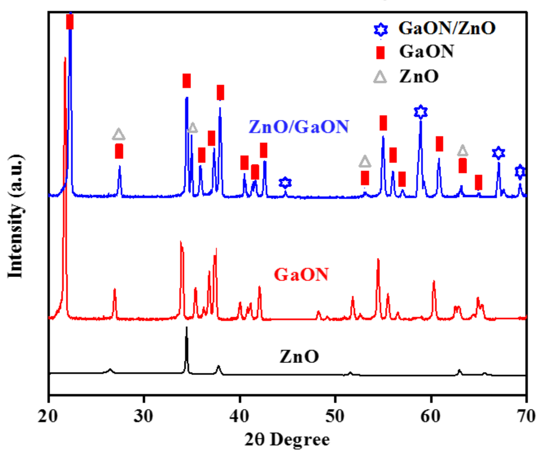
XPS Profiling



XRD Pattern



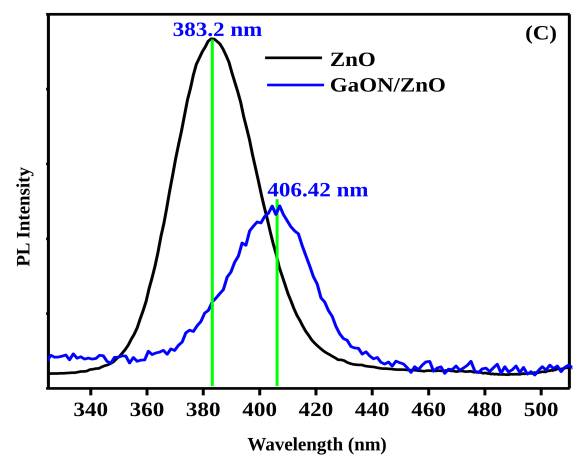
Raman Analysis



Optical Properties of GaON

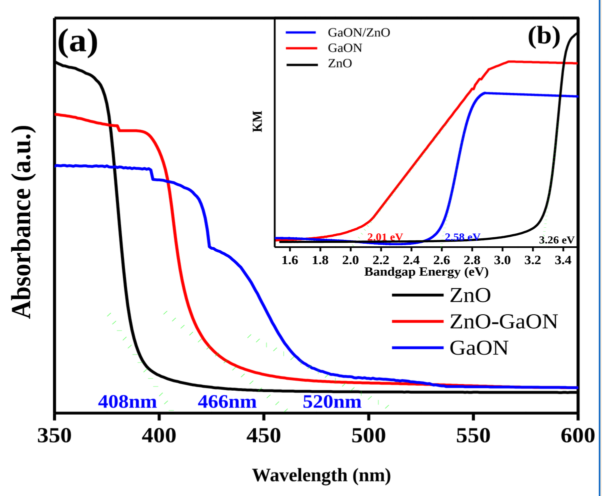
UV-Vis/DRS for bandgap calculations

The PL spectrum showing quenching in the case of GaON/ZnO hybrid, which can be related with the decrease in the rate of photogenerated excitons (holes and electrons) recombination.

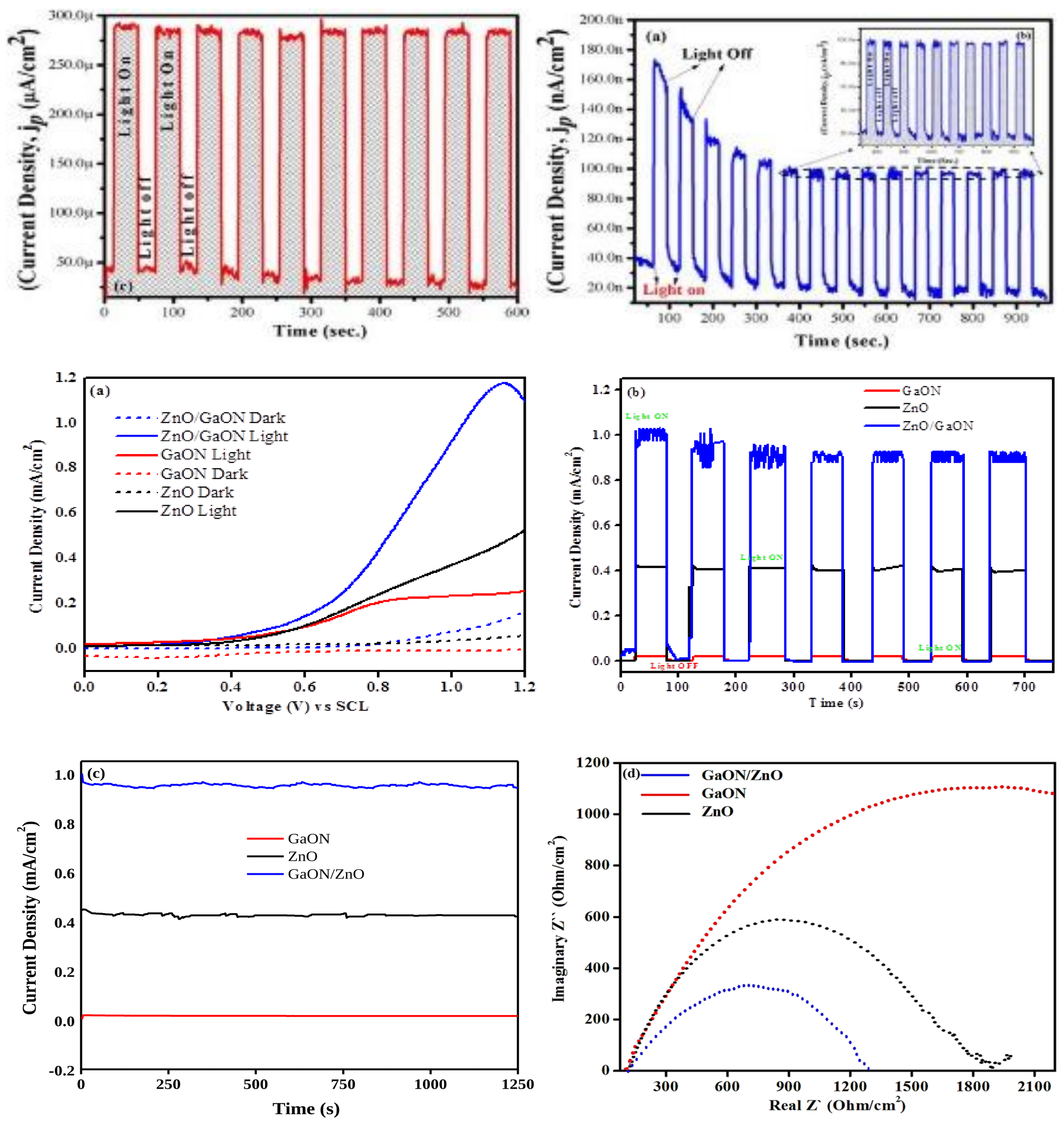


Photoluminescence (PL) Spectra

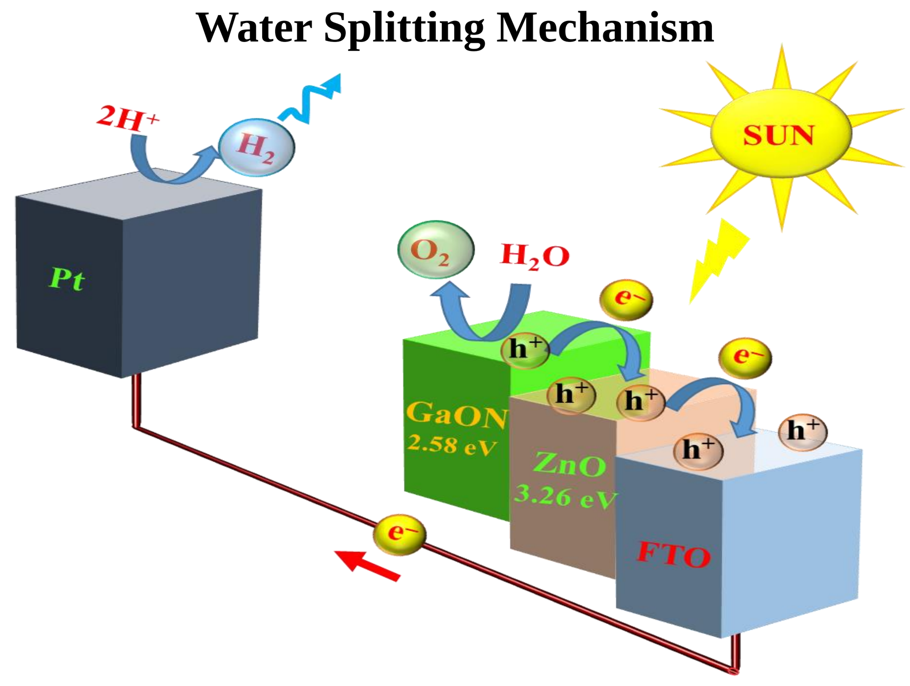
The UV absorption spectrum indicated a red shift towards visible region for GaON/ZnO NAs. The bandgap spectrum (inset) showed value of 2.58 eV, which is suitable for PEC water splitting reactions.



Photocurrent Study



Water Splitting Mechanism



Conclusions and Future Work

- GaON/ZnO hybrid NAs were synthesized and characterized
- The FE-SEM showed the intercalation of GaON within ZnO
- XPS indicate the rich quantity of nitrogen and the Ga-N, Ga-O and other important bond, indicating successful nitridation.
- The XRD and Raman shift showing the formation of the GaON/ZnO heterostructure material.
- Redshift is observed for GaON/ZnO NAs indicating the lowering of bandgap i.e. 2.58 eV.
- Water splitting current density is achieved to be 1.2 mA/cm^2.
- EIS indicated the ease of charge transfer at the interface of GaON/ZnO and electrolytes.
- GaON is nitrogen rich nanomaterial and therefore its composite with other species can be helpful to achieved much improved water splitting reaction. Beside this the same material can also be employed in other photochemical applications.

Acknowledgement

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References

1. Stefan Vajda and Michael G. White ,Catalysis Applications of Size-Selected Cluster Deposition, ACS Catal., 2015, 5 (12), pp 7152–71762.
2. Ke Sun, Matthew T. McDowell, Adam C. Nielander, Shu Hu, Matthew R. Shaner, Fan Yang, Bruce S. Brunschwig, and Nathan S. Lewis. Stable Solar-Driven Water Oxidation to O2(g) by Ni-Oxide-Coated Silicon Photoanodes. J. Phys. Chem. Lett., 2015, 6 (4), pp 592–598.

Contact details

Dr. Ahsanulhaq Qurashi, Associate Professor, Center of Excellence in Nanotechnology, King Fahd University of Petroleum and Minerals, Dhahran 31261, KSA. Email: ahsanulhaq@kfupm.edu.sa.edu