

The review of doctoral thesis

"Hybrid nanomaterials for photoanodes in photoelectrochemical water splitting"

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The thesis explores multifunctional ZnO in various nanoforms as the primary light absorber in multi-component nanocomposite systems. These systems were realized through three established strategies: surface modification, the simultaneous effects of conductive metal coating and gradient impurity element doping, and photosensitization by a narrow-bandgap semiconductor. The adopted methodologies aimed to provide ZnO-based photoanodes with visible light activity and uncover several vital factors affecting photoelectrochemical performance. Advanced spectroscopic and microscopic techniques were employed to comprehensively analyze morphological, crystallographic, optical, and electrical properties and their impact on photoelectrochemical water splitting. The thesis concludes with significant advancements in the understanding of photoanode materials, offering practical insights for developing highly efficient and stable photoelectrodes. This work is poised to make a valuable contribution to the field, addressing the challenges associated with leveraging solar energy for clean and renewable energy production. The following objectives were set in this thesis:

- 1) Synthesis of ZnO nanorods with three different morphologies by hydrothermal growth using polyethyleneimine as a capping agent was realized. The crystallographic, morphological, and optical properties of the resulting distinct morphologies were characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and UV-vis spectroscopy. The impact of morphology on photoanode performance was evaluated by various photoelectrochemical efficiency tests, such as applied bias photon-to-current efficiency (ABPE) and incident photon-to-current conversion efficiency (IPCE).
- 2) Decoration of Au plasmonic nanoparticles on hydrothermally grown ZnO nanorods was attained by photoreduction synthesis and their gradient doping by subsequent heat treatment as visible light active photoanodes. The above-mentioned typical characterization techniques analyzed the produced heterostructure thin films. The photoanode efficiency of the samples was identified by the general characterization method for PEC application.

3) Growing tiny branches around primarily grown nanorods to fabricate ZnO nanodendrites without any assistance from secondary seeding and its photosensitization with BiVO₄ by electrodeposition was accomplished. The type-II heterojunction photoanodes were characterized, and their PEC rankings were determined.

After a thorough reading of the dissertation it can be said that the objectives have been met and the PhD student has successfully dealt with the problems related to this research area.

The thesis is written as a brief review of the current state of knowledge, followed by a concise conclusion of the experimental work and discussion. This type of dissertation was probably chosen (not as monography) due to fact that student published two articles and one submitted in journal related to dissertation's aims (first paper in *Nanoscale Advances* and second in *International Journal of Molecular Sciences*). In addition, the student has co-authored five other publications in the research area covered by the dissertation. From this perspective, his scientific work has undergone peer review, as one would expect in the rigorous peer-review process of reputable journals.

In the experimental section, the procedures for sample preparation, materials and analysis are thoroughly described and the reader can navigate the text well.

Although the results have already been reviewed in internationally respected journals, I would like to take the liberty of having a few comments or questions that the PhD student should answer:

- 1) In the subsection where you discuss the spectra from Raman spectroscopy (page 74), you write that the peaks at 1090 cm⁻¹ and 575 cm⁻¹ are related to defects in ZnO crystals. What defects are you referring to?
- 2) Your dissertation explores various strategies for enhancing the photoelectrochemical performance of ZnO-based photoanodes. Could you discuss any challenges you encountered in synthesizing these hybrid nanomaterials and how these challenges were overcome? Additionally, how do you believe these synthesis techniques could be adapted or improved for large-scale production?
- 3) You investigated multifunctional ZnO in different nanoforms as a primary light absorber. How does the morphology of these nanoforms affect the overall efficiency of the photoelectrochemical water splitting? Can you elaborate on the relationship between specific nanoform structures and their photoelectrochemical performance?
- 4) Considering the advancements made in your research, what future directions do you see for the development of hybrid nanomaterials in photoelectrochemical systems? Are there any

emerging materials or technologies that you believe could significantly impact the efficiency and scalability of photoelectrochemical water splitting?

Dissertation written by Ali Can Güler fully meets the requirements for this type of thesis within the meaning of Act No. 137/2016 Coll. on Higher Education. The student has demonstrated the ability of creative work and independent scientific activity. Therefore, I recommend to accept this thesis for further proceedings and after successful defence to award the Ph.D. (philosophiæ doctor) degree.

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