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High aspect ratio ZnO nanorods for improved photoelectrochemical (PEC) water splitting performances and efficient photocatalytic hydrogen evolution: an integrated experimental and DFT studies

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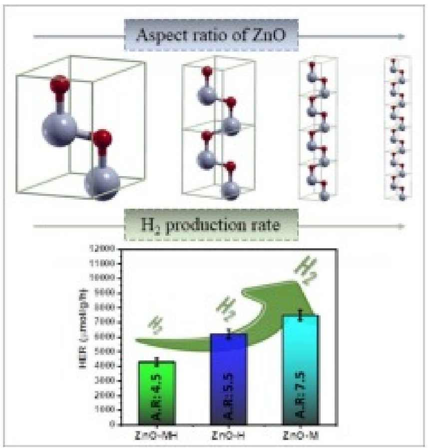
Highlights

- Template/reagents free tuning of aspect ratio of ZnO nanostructures.
- Role of aspect ratio on photocatalytic H_2 production and PEC water splitting.
- Optimal ZnO exhibited outstanding hydrogen evolution rate of 7470.74µmol/g/h.
- DFT validation of high aspect ratio ZnO for H_2 production and PEC water oxidation.

Abstract

Nanostructured ZnO is considered as one of the most prospective photoactive materials, and the primary objective of this work is to tune the morphology and aspect ratio of ZnO without employing any reagents for PEC water splitting and photocatalytic hydrogen evolution applications. TEM and FESEM analyses indicate that the growth of ZnO depend primarily on the synthesis routes alone. ZnO based photoanode exhibits a noticeable structure-dependent performance while assessing their performance in water splitting applications. The designed catalyst composed of microwave-assisted ZnO exhibited superior hydrogen evolution rate of 7470.74µmol/g/h with an apparent quantum yield (AQY) of 55.9%. Similarly, the optimal ZnO nanostructure showed two-times higher oxidation current than the remaining photoanodes at low onset potential of 0.6V Ag/AgCl. This enhancement can be attributed to the uniform growth of ZnO nanorods along the c-axis of ZnO and its high aspect ratio value. The uniformly oriented ZnO nanorods could ensure a direct pathway for electron transport and high active sites, which is also confirmed from DFT (Density Functional Theory) analyses. This unique approach of aspect ratio tuning paves the simplest way for the design of nanostructured materials for energy conversion applications.

Graphical abstract



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Introduction

Over the past few decades, effective utilization of solar energy has become an important topic of research in the field of energy conversion. The conversion of solar energy into solar fuel is the most expedient approach for producing clean energy [1], [2], [3], [4], [5]. Zinc oxide (ZnO) is a common photoanode material used in water splitting because it has higher electron mobility than TiO_2 [6], [7], [8]. Moreover, ZnO has other specific advantages, such as a simple preparation method is required to obtain unique nanostructures, which is favourable for better photon absorption and charge carrier generation [9], [10], [11], [12], [13]. Conversely, the performances recorded using ZnO could not show very promising results during photocatalytic and PEC water splitting. These shortcomings arise from the different issues associated with ZnO. One such specific reason indicated by researchers is the irregular structure of this photoactive materials [14], [15]. ZnO in pristine form often fails to utilize incident photon effectively due to non-unifrom structure, which significantly decreases the efficiency [16]. However, the unsuitable surface morphology may interrupt the light absorption capacity when used as a catalyst in PEC and photocatalytic water splitting applications. Therefore, to enhance the performance of a ZnO-based catalyst, structural tuning should be the ideal trait to maximize the photon absorption capacity [17], [18]. The additional advantage of structural tuning in ZnO also includes flexibility in morphology control with high electron mobility [19], [20]. Recently, one-dimensional (1-D) ZnO nanostructures such as nanorods and nanowires were found to be a very promising material due to their superior electrochemical properties, high exposed surface area, and better optical diffusion length [21], [22], [23]. 1-D ZnO nanostructures have been investigated extensively due to their ability to exhibit high aspect ratio, which are attributed to growth anisotropy towards c-axis. As a result, high aspect ratio ZnO can provide larger number of active sites and corresponding higher activity compared to other nanostructures. Apparently, many of the reported approaches for structural tuning have the drawbacks of morphological deformations, a tedious synthesis process, the usage of external additives or structural templates, etc., which are not demanding for efficient and large-scale applications [24], [25]. Therefore, the optimization of ZnO nanostructure using a low-cost, easy synthesis route may possibly meet the essential requirements of highly efficient water splitting applications.

To improve the performance of ZnO as a catalyst in PEC watersplitting and photocatalytic hydrogen production, this work introduces a simple approach of morphological tuning without using any structural directing reagents. ZnO nanostructures with different aspect ratios were obtained by using three different synthesis methods, namely microwave method, hydrothermal method, and microwave assisted hydrothermal method. All these methods are very useful in providing 1D nanostructures with various aspect ratio, but the same approach is yet to be explored for the dual application in PEC water splitting photocatalytic hydrogen generation. The anisotropic growth induced by different synthesis methods contributes to surface and electronic properties of ZnO that promotes an improved interaction between the carrier components. Moreover, the modified electronic properties of these ZnO nanostructures were also explored using DFT analyses, which is very crucial to understand the electron transfer dynamics through the c-axis oriented ZnO. Therefore, this work demonstrates a simple approach to design structurally tuned ZnO based photoanodes, and the optimal structure is obtained based on their hydrogen production ability and water splitting photocurrent.

Section snippets

Materials and methods

KOH, zinc acetate dihydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$], and ethanol procured from Merck (India) and used as received.

Three different ZnO nanostructures were synthesized following our previously reported work [26]. The molar ratios of $Zn(CH_3COO)_2{\cdot}2H_2O$ and KOH were kept the same (1:15 M ratio) for all three procedures adopted. To begin, a round bottom flask containing 100 ml of deionized water containing solutions of KOH and [$Zn(CH_3COO)_2{\cdot}2H_2O$] was placed inside a microwave oven (LG-domestic microwave) …

Result and discussion

Fig. 1 shows the XRD patterns of the different ZnO nanostructures synthesized using microwave (M), hydrothermal (H), and microwave assisted hydrothermal (MH) methods, respectively. The hexagonal wurtzite phase of ZnO obtained from XRD patterns well matches the JCPDS file no. 36-1451 without involving any impurity phase. The sharp diffraction peaks obtained shows that the as-prepared ZnO nanostructures have a high crystallinity [32]. The size of the crystal is calculated using the (DS) …

Conclusion

Shape-selective ZnO nanostructures with different morphologies have been synthesized by utilizing simple structure-directed reagent free synthesis routes, namely microwave, hydrothermal, and the combination of both methods. During these synthesis methods, other parameters like solvent type and the concentration of the precursor were kept unchanged. The formation and growth mechanisms of different morphologies have been explained in detail. The shape-selective ZnO nanorods have been utilized as …

CRediT authorship contribution statement

Abinash Das: Writing – original draft, Visualization, Validation, Investigation, Data curation, Conceptualization. **Sebin Devasia:** Writing – original draft, Resources, Data curation. **Nisha Banerjee:** Writing – original draft, Formal analysis, Data curation. **Ranjith G. Nair:** Writing – review & editing, Visualization, Supervision, Resources, Project administration, Investigation, Funding acquisition, Formal analysis, Conceptualization. …

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. …

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