Cambridge Centre for Innovation and Development

Nanostructured semiconductors for photoelectrochemical water splitting

Alex Mosquera

Professional Training - Chemical and Biological Engineering

Table of Contents

1. Introduction

The present proposal deals with the improvement of photoelectrochemical water splitting. The purpose of this technology is to produce hydrogen gas, a promising energy carrier given its high energy density and abundance, in a sustainable way. Production of hydrogen in this manner is a useful way of storing solar energy in the form of chemical fuel, which can be used during off peak seasons to produce energy and contribute towards solving the intermittency problem associated with renewable energy sources (Döscher, Young, Geisz, Turner, & Deutsch, 2016). This research aims to increase the Solar-To-Hydrogen efficiency of photoelectrochemical water splitting cells by upgrading the semiconductor electrodes used on these devices. The first strategy to improve the electrodes consists in carrying out research to determine upgrades that can be done on existing materials and to evaluate the development of new materials to be further upgraded at a later stage. In both scenarios, the upgrading methods considered for this research include synthesis of complex nanostructures and use of functional coatings that can improve specific properties of the electrode materials. The goal is to achieve Solar-To-Hydrogen efficiency higher than 10% in order to make it available for commercial purposes (Ma, et al., 2020).

2. Literature review

Energy is one of the core necessities for the progress of societies and new technologies are being investigated to meet its increasing demand in an environmentally friendly manner. Renewable energies are seen as the best alternative to solve this problem, however, energy storage becomes a crucial step to enable their use (Lu, et al., 2020). Storing energy in the form of chemical fuels is seen as one possible solution to this problem, especially in the form of hydrogen gas given its high energy density. Photochemical water splitting has the potential to produce hydrogen in a cost-effective way and with low or zero greenhouse gas emissions (Döscher, Young, Geisz, Turner, & Deutsch, 2016).

Photoelectrochemical water splitting cells consists of a working electrode, which is a semiconductor, a counter electrode and a water-based electrolyte. It operates according to the following working principle. The working electrode is connected to the counter electrode through a metal wire, and they are put in contact with the electrolyte. The working electrode is irradiated with light with photon energy larger than 1.23 eV, which corresponds to the theoretical minimum energy required to split water. This excites electrons that are transferred to the counter electrode via the wire and generates positive charges named holes in the working electrode. The holes oxidize the water and form oxygen gas, and the electrons combine with hydrogen ions to form hydrogen gas (Wang, Ling, Wang, Lu, & Li, 2014).

Various semiconductor materials have been used to manufacture the electrodes of the photoelectrochemical cells such as metal oxides, metal nitrides, metal oxynitrides, phosphides, and silicon. Among these materials, metal oxynitrides are seen as a promising option since they combine properties of oxides and nitrides. They have the appropriate band gap to be active in the wavelength of visible light and the potential to harness solar energy more efficiently (Ahmed & Xinxin, 2016). Both metal nitrides and metal oxynitrides are suitable for electrochemical cells given their high conductivity and corrosion resistance that provides them with high activity and durability. Their structure also facilitates charge transfer (Dutta, Indra, Feng, Han, & Song, 2019).

3. Research aims

General objectives

- Synthesize semiconductor electrodes using metal oxynitride nanostructures and integrate the materials into photoelectrochemical cells for solar water splitting into hydrogen and oxygen.

- Improve the performance of photoelectrochemical cells by applying different strategies in the synthesis of semiconductor electrodes.

Specific objectives

- Evaluate the performance of electrodes and find the elements that provide the best properties.

- Study different fabrication techniques and analyze how the complexity of the nanostructures influence the performance of the semiconductor electrode.

- Modify the surface of the electrodes with functional coating depending on the properties that need further improvement in order to achieve the 10% Solar-To-Hydrogen efficiency required for commercial purposes.

4. Methodology

To address the objectives mentioned above, the first step would be carrying out a literature survey about metal oxynitrides that have already been studied in order to determine if it is better to try different strategies to improve current materials or to analyse the possibility of working with materials that have not been studied before.

The next step is to study the electronic structure of the chosen materials using Density Functional Theory calculations that can be done on commercial software such as VASP or open source software such as Python and compare the computational theoretical results with experimental results (Ma, et al., 2021).

After gaining understanding of their electronic structure, metal oxynitrides will be used to fabricate electrodes using methods that will yield different nanostructure arrays and characterized using analytical techniques such as electron microscopy (TEM and SEM) to evaluate the morphology and the effect of the fabrication method on the complexity of the nanostructures and the performance of the electrode (Salem, Mokhtar, Abdelhafiz, & Allam, 2020).

The electrochemical performance of the fabricated electrodes will be measured using techniques that include electrochemical impedance spectroscopy (EIS), linear square voltammetry (LSV) and chronoamperometry (CA) curves, Mott-Schottky characterization and open circuit photovoltages (OCPV) as suggested in previous research. The electrochemical properties will be measured using a conventional three electrode (working, counter and reference electrodes) setup and a light source. (Lu, et al., 2020).

The performance of the electrodes can then be improved with the use of functional coating. The materials to coat the electrodes will be chosen after analyzing which properties need to be enhanced. Functional coatings have shown to provide various upgrades such as increase electroconductivity, provide thermal and chemical stability, reduce photocorrosion, increase water oxidation kinetics, or enhance charge separation (Landsmann, et al., 2016). The properties will be improved with the aim of achieving Solar-To-Hydrogen efficiency higher than the 10% required to reach commercial scale (Ma, et al., 2020).

5. Timescale

The timescale with the milestones of the research project is presented as a Gantt diagram in Table 1.

Table 1. Timescale of the research project

Activities	Month	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Choose Research Topic		■	■																																																										
Literature Review				■	■	■	■																																																						
Establish Objectives						■	■																																																						
Write Research Proposal								■	■	■	■																																																		
Creation of Material Database												■	■	■	■																																														
Selection of Materials															■	■																																													
Electronic Structure Studies																	■	■	■																																										
Computational Theoretical Results																				■	■																																								
Experimental Comparison																						■	■	■	■																																				
Material Synthesis																										■	■	■	■																																
Material Characterization																														■	■																														
Evaluate synthesis methods																																■	■	■	■																										
Test Electrochemical Performance																																				■	■	■	■																						
Analyze Improvement Strategies																																							■	■	■	■																			
Test Improvement Strategies																																										■	■	■	■																
Test Electrochemical Performance																																														■	■														
Cost Evaluation																																																■	■												
Water Splitting Economic Analysis																																																		■	■	■	■								
Results Discussion																																																						■	■	■					
Conclusions and Recommendations																																																								■	■	■			
Publication of Results																																																											■	■	■

6. References

Ahmed, M., & Xinxin, G. (2016). A review of metal oxynitrides for photocatalysis. *Inorganic Chemistry Frontiers, 3*(5), 578-590.

Döscher, H., Young, J., Geisz, J., Turner, J., & Deutsch, T. (2016). Solar-to-hydrogen efficiency: Shining light on photoelectrochemical device performance. *Energy & Environmental Science, 9*, 74-80.

Dutta, S., Indra, A., Feng, Y., Han, H., & Song, T. (2019). Promoting electrocatalytic overall water splitting with nanohybrid of transition metal nitride-oxynitride. *Applied Catalysis B: Environmental, 241*, 521-527.

Landsmann, S., Surace, Y., Trottmann, M., Dilger, S., Weidenkaff, A., & Pokrant, S. (2016). Controlled Design of Functional Nano-Coatings: Reduction of Loss Mechanisms in Photoelectrochemical Water Splitting. *Applied Materials & Interfaces, 8*(19), 12149-12157.

Lin, Y., Yuan, G., Liu, R., Zhou, S., Sheehan, S., & Wang, D. (2011). Semiconductor nanostructure-based photoelectrochemical water splitting: A brief review. *Chemical Physics Letters, 507*(4-6), 209-215.

Lu, C., Jothi, P., Thersleff, T., Budnyak, T., Rokicinska, A., Yubuta, K., . . . Slabon, A. (2020). Nanostructured core–shell metal borides–oxides as highly efficient electrocatalysts for photoelectrochemical water oxidation. *Nanoscale, 12*(5), 3121-3128.

Ma, Z., Chen, K., Jaworski, A., Chen, J., Rokicińska, A., Kuśtrowski, P., . . . Slabon, A. (2021). Structural Properties of NdTiO2+xN1−x and Its Application as Photoanode. *Inorganic Chemistry, 60*(2), 919-929.

Ma, Z., Piętak, K., Piątek, J., Reed, J., Rokicińska, A., Kuśtrowski, P., . . . Slabon, A. (2020). Semi-transparent quaternary oxynitride photoanodes on GaN underlayers. *Chemical Communications, 56*(86), 13193-13196.

Salem, K., Mokhtar, A., Abdelhafiz, A., & Allam, N. (2020). Niobium–Zirconium Oxynitride Nanotube Arrays for Photoelectrochemical Water Splitting. *Applied Nano Materials, 3*(6), 6078-6088.

Wang, G., Ling, Y., Wang, H., Lu, X., & Li, Y. (2014). Chemically modified nanostructures for photoelectrochemical water splitting. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 19*, 35-51.