## Electrochemical fabrication and reductive Li-doping of TiO<sub>2</sub>/ERGO nanocomposite as photoanode for photoelectrochemical water-splitting

Zeynep Selin BAŞARAN YILMAZ<sup>1</sup>, Ekin AKYÜREK<sup>1</sup> and Ümit DEMİR<sup>1</sup>

<sup>1</sup>Department of Chemistry, Faculty of Sciences, Gebze Technical University, Gebze/Kocaeli, Turkey

Production of H<sub>2</sub> as a sustainable and clean energy source by photocatalytic or photoelectrochemical water splitting is one of the most promising ways to solve the problems of energy and environmental pollution. TiO2 has been one of the most researched materials as a photocatalyst in the photocatalytic water-splitting into H<sub>2</sub> and O<sub>2</sub>. It is used in solar cells, batteries, supercapacitors, the removal of air and water pollution, and water-splitting into H<sub>2</sub> as a photocatalyst[1]. Also, TiO<sub>2</sub> combined with graphene derivatives has become a great research interest as potential photoanode material for diverse applications in photocatalysis and solar energy conversion due to providing high surface area and improving carrier mobility.

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In this study, it was aimed to fabricate a photoanode that can operate in the entire spectrum of the sun for effective photoelectrochemical water-splitting by shifting with electrochemical reductive self-doping the wide band gap of TiO<sub>2</sub>/ERGO nanocomposite which produced by coelectrodeposition technique which is a simple, one-pot, and environmentally friendly directly on FTO. TiO2/ERGO nanocomposites were doped as electrochemically reductive in the presence of  $Li^{\scriptscriptstyle +}$  cations to form  $Ti^{3\scriptscriptstyle +}$  defects and Ovacancies in the structure[2]. Then these doped electrodes were characterized by XRD, XPS, and FESEM techniques in terms of composition, structure, and morphology. The improvement in photoelectrochemical efficiency of the doped TiO<sub>2</sub>/ERGO structures in the visible region was determined by photocurrent density measurements, UV-vis-DRS, and EIS techniques. Then, Li-doped TiO2/ERGO-FTO photoanodes with high activity under visible light will be used in the production of H<sub>2</sub> gas by photoelectrochemical water-splitting without any bias-voltage.



Figure 1. Determination of photoactivity of Li-TiO<sub>2</sub>/ERGO-FTO photoelectrodes in water-splitting.

FESEM images of the Li-TiO2/ERGO electrode prepared by reduction from the LiClO<sub>4</sub> solution are given in Fig. 2a. It was observed that the nanocomposite structure consisting of TiO<sub>2</sub> and graphene did not deteriorate and was preserved exactly after Li-doping.



## Figure 2. FESEM images of Li-TiO<sub>2</sub>/ERGO (a) and photocurrent responses in 0.5 M KOH of TiO2/ERGO and Li-TiO<sub>2</sub>/ERGO photoelectrodes (b)

Photocurrent response of photocatalysts as shown in Fig. 2b, in a 3-electrode cell where the Pt electrode is used as the counter, Ag/AgCl electrode as the reference and the Li-TiO<sub>2</sub>/ERGO-FTO nanocomposite electrode as the photoanode, in 0.5 M KOH aqueous solution, the photoanode in the solar simulator (AM1.5G, 100mWcm<sup>-2</sup>) and the resulting photocurrent was measured with a potentiostat depending on time (I-t). Almost 10-fold increase in photocurrent densities was observed after electrochemical reductive doping.

It is expected that Li-TiO<sub>2</sub>/ERGO-FTO nanocomposites will reach 25 µmol.h<sup>-1</sup>cm<sup>-2</sup> solar-hydrogen conversion (STH) efficiency in the visible region for water-splitting as photoanode.

## Acknowledgements

This study was financially supported by the Scientific and Technological Research Council of Turkey (TUBITAK, Project Number: 122Z028).

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Res. Assist. Zeynep Selin Başaran Yılmaz obtained her B.S. and M.S. degrees in Chemistry from Istanbul Technical University and Gebze Technical University, Turkey in 2018 and 2022. She is currently a Ph.D candidate at the Department of Chemistry, Gebze Technical University. Her research interest covers of photoelectrochemical water-splitting, metal-oxide/graphene nanocomposites and dye sensitized solar cells.

Presentating author: Zeynep Selin Başaran Yılmaz, e-mail: zsbasaran@gtu.edu.tr tel: +90 538 8565194