## **1. Introduction**

In the present century, there is quite an extensive diversity of hazards involved with growing energy consumption along with increasing population and improving industrialization [1]. Of course, there are potential risks regarding carbon footprint, greenhouse gases, and global warming; the underlying fact is that fossil fuels have irreparable damages to the environment and its shortage must be considered the main objection. The consequential way to tackle this problem is conventional fossil fuels alternate with bio-friendly energy resources. Having increased society's demand, the research is focused on design and organization power sources devices. To fulfill such targets, the main aspect of efforts is producing energy in a greener pathway, as well as storage energy through cost-effective devices for widespread utilization [2]. Producing hydrogen from water is attractive because, in contrast to fossil fuel, it is renewable and bio-friendly, which omits releasing greenhouse gases [3]. Produced hydrogen can be stored in liquid and gaseous, and solidstate phase; the fact is high-pressure compression and liquefaction process is the most impractical aspect of storing hydrogen in liquid and gaseous phase [4] which turn the view to store hydrogen by physisorption process in nanostructured materials, such as carbonaceous and metal organic framework (MOF) [4, 5]. Based on physisorption, the hydrogen spillover mechanism was extensively used in literature by carbon materials [6], zeolites [7], and MOF [8, 9]. In the spillover process, hydrogen dissociation source, receptor and connection are critical factors [10]. Highly distributed metals (hydrogen dissociation source) contribute to increase metal surface area and provide the adequate connection between metal and carbon receptors [10]. It is worth mentioning that the metal NPs overloading adversely affected; the optimized loading was achieved when the surface of the receptor is mainly accessible [11-14]. An excellent receptor provides more host sites

for hydrogen adsorption; modification of surface chemistry (doping of receptor by boron, nitrogen) was suggested for improving the surface area. Comparing adding oxygen functional groups documented that surface oxygen groups stabilize the hydrogen and offer bridges [15-17], as a consequence hydrogen atoms can diffuse to the receptor's host site which were inaccessible before [17, 18]. In addition, oxygen functional groups, such as hydroxyl groups, increase hydrophilicity which offer the most effective property for interaction between materials' surface and liquid [19]. The last but not the least factor has been investigated to fulfill intimate contact, the physical loading of metal or metal oxide on carbon receptors suggested as an easiest way to overcome lack of bridges between hydrogen dissociation source and receptor [11, 20, 21].

Graphene oxide (GO), which has a large surface area and different functional groups, is a good candidate as a substrate in various research fields; for instance, catalytic activity [22-25] and energy-storing [26-28]. An overview of the literatures indicates that different components have modified GO as hydrogen storage substrate [29-38]. GO's plate offers good space for hydrogen adsorption, diffusion and storage, besides oxygen functional groups, such as hydroxyl groups, accelerate adsorption of hydrogen on carbon surface materials, [39]. Raising hydrogen storage capacity was achieved by modifying surface's oxygen groups in some ways, among others adding transition metal[40, 41] and metal oxides like TiO<sub>2</sub>, ZnO, and ZrO<sub>2</sub> [42-45] is the most convenient way; which could improve the surface area and electrochemical performance [46]. Having unique mechanical, thermal, and structural properties, zirconia (ZrO<sub>2</sub>) has been utilized in a diverse range of fields [47]. Metal NPs were exceedingly utilized as adsorbent species in hydrogen storage [1, 28, 41, 48-53]; decorating substrate with nanoparticles is an effective way to promote applications that are unattainable by substrate individually. According to specific properties of Au NPs, it has been used as an improving agent in catalyst application [54, 55], hydrogen production [48, 56, 57]

and analytical sensitivity [58]. The approaches to decorate substrate with Au NPs are different in literature: chemical deposition[59], seed-mediated growth [60] and laser ablation in liquid (LAL) [25, 61]; the last one has attracted attention because of its adjustable parameters and eliminating contaminating reagents[62]. Besides, LAL is a physical method to generate NPs by different shapes and morphology[63]. Among deposition methods, electrophoretic deposition (EPD) was extensively used down to its adjustability in parameters and deposition quality [24]. EPD was considered as an effective method for deposition nanocomposite on conductive substrate [64], and these electrodes have the potential to employ in different applications: catalyst substrate [24], oilwater separation [65], anticorrosion industries [66], and ethanol electro-oxidation [67]. Electrochemical hydrogen storage through cyclic voltammetry (CV) is a prevailing method to study adsorption/desorption of hydrogen in detail [1]. Water decomposition was taken place in cathodic direction; consequently, hydrogen was produced from water. The hydrogen atoms are migrated to the surface of electrodes under applying potential and desorbed in anodic sweep [1].

Considering consensus regarding environmental-friendly methods leads us to introduce a new nanocomposite close to this target by using GO as a substrate. To investigate the effect of oxygen functional group on hydrogen storage, zirconia NPs were physically loaded on GO's surfaces via the reflux route. The decorated nanocomposite with Au NPs was accomplished by LAL method to prove Au NPs' influence on hydrogen adsorption performance. Nanocomposites were deposited on stainless steel mesh, a conductive substrate, by EPD, and CV was deployed to assess hydrogen storage on working electrodes in an alkaline medium.

## References

[1] B. Feizi Mohazzab, B. Jaleh, M. Nasrollahzadeh, S. Khazalpour, M. Sajjadi, and R.S. Varma, Upgraded Valorization of Biowaste: Laser-Assisted Synthesis of Pd/Calcium Lignosulfonate Nanocomposite for Hydrogen Storage and Environmental Remediation, ACS omega. (2020).

[2] H. Wang, H. Zhang, Z. Wang, X. Xia, Y. Bao, K. Homewood, M.d.A. Lourenço, G. Shao, and Y. Gao, In-situ hydrogen production and storage in (002) oriented TiO<sub>2</sub> thin films, Applied Surface Science. 509 (2020) 145366.

[3] L. Grinberga, J. Hodakovska, J. Kleperis, G. Vaivars, and J. Klavins, Electrochemical hydrogen storage and usage aspects: Nickel electrode in acidic electrolyte, Russian Journal of Electrochemistry. 43 (2007) 598-602.

[4] N. Rusman, and M. Dahari, A review on the current progress of metal hydrides material for solid-state hydrogen storage applications, International Journal of Hydrogen Energy. 41 (2016) 12108-12126.

[5] K. Shashikala, Hydrogen storage materials, Functional Materials Preparation. Process. Appl. 15 (2012) 607-637.

[6] A.J. Lachawiec, G. Qi, and R.T. Yang, Hydrogen storage in nanostructured carbons by spillover: bridge-building enhancement, Langmuir. 21 (2005) 11418-11424.

[7] Y. Li, and R.T. Yang, Hydrogen storage in low silica type X zeolites, The Journal of Physical Chemistry B. 110 (2006) 17175-17181.

[8] Y. Li, and R.T. Yang, Significantly enhanced hydrogen storage in metal– organic frameworks via spillover, Journal of the American Chemical Society. 128 (2006) 726-727.

[9] Y. Li, and R.T. Yang, Hydrogen storage in metal– organic frameworks by bridged hydrogen spillover, Journal of the American Chemical Society. 128 (2006) 8136-8137.

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[10] L. Wang, and R.T. Yang, Hydrogen storage on carbon-based adsorbents and storage at ambient temperature by hydrogen spillover, Catalysis Reviews. 52 (2010) 411-461.

[11] L. Wang, and R.T. Yang, Hydrogen storage properties of carbons doped with ruthenium, platinum, and nickel nanoparticles, The Journal of Physical Chemistry C. 112 (2008) 12486-12494.

[12] K.-Y. Lin, W.-T. Tsai, and T.-J. Yang, Effect of Ni nanoparticle distribution on hydrogen uptake in carbon nanotubes, Journal of Power Sources. 196 (2011) 3389-3394.

[13] C.-K. Back, G. Sandí, J. Prakash, and J. Hranisavljevic, Hydrogen sorption on palladiumdoped sepiolite-derived carbon nanofibers, The Journal of Physical Chemistry B. 110 (2006) 16225-16231.

[14] B.-J. Kim, Y.-S. Lee, and S.-J. Park, Preparation of platinum-decorated porous graphite nanofibers, and their hydrogen storage behaviors, Journal of colloid and interface science. 318 (2008) 530-533.

[15] L. Wang, F.H. Yang, R.T. Yang, and M.A. Miller, Effect of surface oxygen groups in carbons on hydrogen storage by spillover, Industrial & engineering chemistry research. 48 (2009) 2920-2926.

[16] J. Carter, P. Lucchesi, P. Corneil, D. Yates, and J. Sinfelt, Exchange of deuterium with the hydroxyl groups of alumina, The Journal of Physical Chemistry. 69 (1965) 3070-3074.

[17] Q. Li, and A.D. Lueking, Effect of surface oxygen groups and water on hydrogen spillover in Pt-doped activated carbon, The Journal of Physical Chemistry C. 115 (2011) 4273-4282.

[18] W.J. Ambs, A. WJ, and M. MM JR, Hydrogen spillover on platinum-alumina, effect of water, (1983).

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[19] J. Miller, B. Meyers, F. Modica, G. Lane, M. Vaarkamp, and D. Koningsberger, Hydrogen temperature-programmed desorption (H<sub>2</sub> TPD) of supported platinum catalysts, Journal of Catalysis. 143 (1993) 395-408.

[20] A.C. Cooper, and G.P. Pez, Hydrogen storage using carbon-metal hybrid compositions, in, Google Patents, 2003.

[21] A. Lueking, and R.T. Yang, Hydrogen spillover from a metal oxide catalyst onto carbon nanotubes—implications for hydrogen storage, Journal of Catalysis. 206 (2002) 165-168.

[22] M. Nasrollahzadeh, B. Jaleh, T. Baran, and R.S. Varma, Efficient degradation of environmental contaminants using Pd-RGO nanocomposite as a retrievable catalyst, Clean Technologies and Environmental Policy. 22 (2020) 325-335.

[23] P.T. Ahmad, B. Jaleh, M. Nasrollahzadeh, and Z. Issaabadi, Efficient reduction of waste water pollution using  $GO/\gamma MnO_2/Pd$  nanocomposite as a highly stable and recoverable catalyst, Separation and Purification Technology. 225 (2019) 33-40.

[24] B. Feizi Mohazzab, B. Jaleh, Z. Issaabadi, M. Nasrollahzadeh, and R.S. Varma, Stainless steel mesh-GO/Pd NPs: catalytic applications of Suzuki–Miyaura and Stille coupling reactions in eco-friendly media, Green Chemistry. 21 (2019) 3319-3327.

[25] B. Clean Technologies and Environmental PolicyFeizi Mohazzab, B. Jaleh, M. Nasrollahzadeh, Z. Issaabadi, and R.S. Varma, Laser ablation-assisted synthesis of  $GO/TiO_2/Au$  nanocomposite: Applications in K<sub>3</sub> [Fe (CN)<sub>6</sub>] and Nigrosin reduction, Molecular Catalysis. 473 (2019) 110401.

[26] T. Kuila, A.K. Mishra, P. Khanra, N.H. Kim, and J.H. Lee, Recent advances in the efficient reduction of graphene oxide and its application as energy storage electrode materials, Nanoscale. 5 (2013) 52-71. [27] K. Sekar, G. Raji, L. Tong, Y. Zhu, S. Liu, and R. Xing, Boosting the electrochemical performance of MoS<sub>2</sub> nanospheres-N-doped-GQDs-rGO three-dimensional nanostructure for energy storage and conversion applications, Applied Surface Science. 504 (2020) 144441.

[28] M.D. Ganji, S. Emami, A. Khosravi, and M. Abbasi, Si-decorated graphene: a promising media for molecular hydrogen storage, Applied Surface Science. 332 (2015) 105-111.

[29] P. Bénard, and R. Chahine, Modeling of adsorption storage of hydrogen on activated carbons, International Journal of Hydrogen Energy. 26 (2001) 849-855.

[30] S.H. Aboutalebi, S. Aminorroaya-Yamini, I. Nevirkovets, K. Konstantinov, and H.K. Liu, Enhanced hydrogen storage in graphene oxide-MWCNTs composite at room temperature, Advanced Energy Materials. 2 (2012) 1439-1446.

[31] C.-C. Huang, N.-W. Pu, C.-A. Wang, J.-C. Huang, Y. Sung, and M.-D. Ger, Hydrogen storage in graphene decorated with Pd and Pt nano-particles using an electroless deposition technique, Separation and purification technology. 82 (2011) 210-215.

[32] V.B. Parambhath, R. Nagar, and S. Ramaprabhu, Effect of nitrogen doping on hydrogen storage capacity of palladium decorated graphene, Langmuir. 28 (2012) 7826-7833.

[33] Y. Wang, C.X. Guo, X. Wang, C. Guan, H. Yang, K. Wang, and C.M. Li, Hydrogen storage in a Ni–B nanoalloy-doped three-dimensional graphene material, Energy & Environmental Science. 4 (2011) 195-200.

[34] E.S. Cho, A.M. Ruminski, S. Aloni, Y.-S. Liu, J. Guo, and J.J. Urban, Graphene oxide/metal nanocrystal multilaminates as the atomic limit for safe and selective hydrogen storage, Nature communications. 7 (2016) 1-8.

[35] G. Wu, J. Li, C. Tang, T. Ouyang, C. He, C. Zhang, and J. Zhong, A comparative investigation of metal (Li, Ca and Sc)-decorated 6, 6, 12-graphyne monolayers and 6, 6, 12-graphyne nanotubes for hydrogen storage, Applied Surface Science. 498 (2019) 143763.

[36] N. Naseri, S. Ghasemi, M. Pourreza, and A. Moshfegh, Sustainable starfish like cobalt electrocatalyst grown on optimized CNT-graphene hybrid host for efficient water oxidation, Applied Surface Science. (2020) 146391.

[37] Z. Li, D. Wu, Y. Ouyang, H. Wu, M. Jiang, F. Wang, and L.Y. Zhang, Synthesis of hollow cobalt phosphide nanocrystals with ultrathin shells anchored on reduced graphene oxide as an electrocatalyst toward hydrogen evolution, Applied Surface Science. 506 (2020) 144975.

[38] J. Zhao, D. Zhang, F. Guo, H. Guo, Y. Liu, Y. Yin, H. Hu, and X. Wang, Facile one-pot supercritical synthesis of MoS<sub>2</sub>/pristine graphene nanohybrid as a highly active advanced electrocatalyst for hydrogen evolution reaction, Applied Surface Science. (2020) 147282.

[39] R. Krishna, E. Titus, L.C. Costa, J.C. Menezes, M.R. Correia, S. Pinto, J. Ventura, J. Araújo, J.A. Cavaleiro, and J.J. Gracio, Facile synthesis of hydrogenated reduced graphene oxide via hydrogen spillover mechanism, Journal of materials chemistry. 22 (2012) 10457-10459.

[40] V. Jain, and B. Kandasubramanian, Functionalized graphene materials for hydrogen storage, Journal of Materials Science. (2020) 1-39.

[41] W. Zhang, Z. Zhang, F. Zhang, and W. Yang, Ti-decorated graphitic-C<sub>3</sub>N<sub>4</sub> monolayer: A promising material for hydrogen storage, Applied Surface Science. 386 (2016) 247-254.

[42] M. Kaur, and K. Pal, An investigation for hydrogen storage capability of zirconia-reduced graphene oxide nanocomposite, International Journal of Hydrogen Energy. 41 (2016) 21861-21869.

[43] M. Onyszko, K. Urbas, M. Aleksandrzak, and E. Mijowska, Reduced graphene oxide and inorganic nanoparticles composites–synthesis and characterization, Polish Journal of Chemical Technology. 17 (2015) 95-103.

[44] S.-R. Yan, T. Gholami, O. Amiri, M. Salavati-Niasari, S. Seifi, M. Amiri, M. Sabet, and L.K. Foong, Effect of adding TiO<sub>2</sub>, SiO<sub>2</sub> and graphene on of electrochemical hydrogen storage performance and coulombic efficiency of CoAl<sub>2</sub>O<sub>4</sub> spinel, Journal of Alloys and Compounds. 828 (2020) 154353.

[45] P. Pei, M.B. Whitwick, S. Kureshi, M. Cannon, G. Quan, and E. Kjeang, Hydrogen storage mechanism in transition metal decorated graphene oxide: The symbiotic effect of oxygen groups and high layer spacing, International Journal of Hydrogen Energy. 45 (2020) 6713-6726.

[46] Y. Zhang, Y. Ji, W. Zhang, F. Hu, Y. Qi, and D. Zhao, Electrochemical hydrogen storage behaviors of as-milled Mg-Ce-Ni-Al-based alloys applied to Ni-MH battery, Applied Surface Science. 494 (2019) 170-178.

[47] W.L.N. Bandara, R.M. de Silva, K.N. de Silva, D. Dahanayake, S. Gunasekara, and K. Thanabalasingam, Is nano  $ZrO_2$  a better photocatalyst than nano  $TiO_2$  for degradation of plastics?, RSC advances. 7 (2017) 46155-46163.

[48] S. Jo, P. Verma, Y. Kuwahara, K. Mori, W. Choi, and H. Yamashita, Enhanced hydrogen production from ammonia borane using controlled plasmonic performance of Au nanoparticles deposited on TiO<sub>2</sub>, Journal of Materials Chemistry A. 5 (2017) 21883-21892.

[49] H.-S. Kim, H. Lee, K.-S. Han, J.-H. Kim, M.-S. Song, M.-S. Park, J.-Y. Lee, and J.-K. Kang, Hydrogen storage in Ni nanoparticle-dispersed multiwalled carbon nanotubes, The Journal of Physical Chemistry B. 109 (2005) 8983-8986. [50] E. Yoo, L. Gao, T. Komatsu, N. Yagai, K. Arai, T. Yamazaki, K. Matsuishi, T. Matsumoto, and J. Nakamura, Atomic hydrogen storage in carbon nanotubes promoted by metal catalysts, The Journal of Physical Chemistry B. 108 (2004) 18903-18907.

[51] L. Ma, J.-M. Zhang, and K.-W. Xu, Hydrogen storage on nitrogen induced defects in palladium-decorated graphene: a first-principles study, Applied surface science. 292 (2014) 921-927.

[52] Y. Wang, Z. Meng, Y. Liu, D. You, K. Wu, J. Lv, X. Wang, K. Deng, D. Rao, and R. Lu, Lithium decoration of three dimensional boron-doped graphene frameworks for high-capacity hydrogen storage, Applied Physics Letters. 106 (2015) 063901.

[53] Y.-J. Han, and S.-J. Park, Influence of nickel nanoparticles on hydrogen storage behaviors of MWCNTs, Applied Surface Science. 415 (2017) 85-89.

[54] B. Feizi Mohazzab, B. Jaleh, M. Nasrollahzadeh, Z. Issaabadi, and R.S. Varma, Laser ablation-assisted synthesis of GO/TiO2/Au nanocomposite: Applications in  $K_3$ [Fe (CN)<sub>6</sub>] and Nigrosin reduction, Molecular Catalysis. 473 (2019) 110401.

[55] A. Nasri, B. Jaleh, Z. Nezafat, M. Nasrollahzadeh, S. Azizian, H.W. Jang, and M. Shokouhimehr, Fabrication of g-C3N4/Au nanocomposite using laser ablation and its application as an effective catalyst in the reduction of organic pollutants in water, Ceramics International. (2020).

[56] M. Eslamipanah, B. Jaleh, B.F. Mohazzab, S. Khazalpour, M. Nasrollahzadeh, and M. Shokouhimehr, Facile synthesis and electrochemical hydrogen storage of bentonite/TiO2/Au nanocomposite, International Journal of Hydrogen Energy. (2020).

[57] A. Nasri, B. Jaleh, S. Khazalpour, M. Nasrollahzadeh, and M. Shokouhimehr, Facile synthesis of graphitic carbon nitride/chitosan/Au nanocomposite: A catalyst for electrochemical hydrogen evolution, International Journal of Biological Macromolecules. 164 (2020) 3012-3024.

[58] V. Mani, B.V. Chikkaveeraiah, V. Patel, J.S. Gutkind, and J.F. Rusling, Ultrasensitive immunosensor for cancer biomarker proteins using gold nanoparticle film electrodes and multienzyme-particle amplification, ACS nano. 3 (2009) 585-594.

[59] L. Cheng, D. Zhang, Y. Liao, F. Li, H. Zhang, and Q. Xiang, Constructing functionalized plasmonic gold/titanium dioxide nanosheets with small gold nanoparticles for efficient photocatalytic hydrogen evolution, Journal of colloid and interface science. 555 (2019) 94-103.

[60] Y.-J. Kim, J. Park, H.S. Jeong, M. Park, S. Baik, D.S. Lee, H. Rho, H. Kim, J.H. Lee, and S.-M. Kim, A seed-mediated growth of gold nanoparticles inside carbon nanotube fibers for fabrication of multifunctional nanohybrid fibers with enhanced mechanical and electrical properties, Nanoscale. 11 (2019) 5295-5303.

[61] W. Zhu, X. Li, W. Liu, Z. Chen, J. Li, and H. Pan, In situ Growth of Gold Nanoparticles Based on Simultaneous Green Reduction by Methylene Blue for Non-Enzymatic Glucose Sensing, Int. J. Electrochem. Sci. 12 (2017) 4970-4978.

[62] B. Jaleh, S. Karami, M. Sajjadi, B.F. Mohazzab, S. Azizian, M. Nasrollahzadeh, and R.S. Varma, Laser-assisted preparation of Pd nanoparticles on carbon cloth for the degradation of environmental pollutants in aqueous medium, Chemosphere. 246 (2020) 125755.

[63] A. Serkov, E. Barmina, A. Simakin, P. Kuzmin, V. Voronov, and G. Shafeev, Generation of core–shell nanoparticles Al@ Ti by laser ablation in liquid for hydrogen storage, Applied Surface Science. 348 (2015) 71-74.

[64] I. Corni, M.P. Ryan, and A.R. Boccaccini, Electrophoretic deposition: From traditional ceramics to nanotechnology, Journal of the European Ceramic Society. 28 (2008) 1353-1367.

[65] B. Jaleh, K. Shariati, M. Khosravi, A. Moradi, S. Ghasemi, and S. Azizian, Uniform and stable electrophoretic deposition of graphene oxide on steel mesh: Low temperature thermal treatment for switching from superhydrophilicity to superhydrophobicity, Colloids and Surfaces A: Physicochemical and Engineering Aspects. 577 (2019) 323-332.

[66] S. Majidi, B. Jaleh, B. Feizi Mohazzab, M. Eslamipanah, and A. Moradi, Wettability of Graphene Oxide/Zinc Oxide Nanocomposite on Aluminum Surface Switching by UV Irradiation and Low Temperature Annealing, Journal of Inorganic and Organometallic Polymers and Materials. (2020) 1-11.

[67] A.A. Daryakenari, D. Hosseini, T. Saito, A. Apostoluk, C.R. Müller, and J.-J. Delaunay, Ethanol electro-oxidation on nanoworm-shaped Pd particles supported by nanographitic layers fabricated by electrophoretic deposition, RSC Advances. 5 (2015) 52578-52587.

[68] W.S. Hummers Jr, and R.E. Offeman, Preparation of graphitic oxide, Journal of the american chemical society. 80 (1958) 1339-1339.