

3.2. Cyclic voltammetry study

Aiming to assess hydrogen storage, CV was carried out at room temperature in alkaline electrolyte through prefabricated electrodes; influence of TiO₂ and Au NPs on hydrogen storage capacity was under surveyed versus initial bentonite. Firstly, in order to determine the electrode with the highest hydrogen storage capacity, the working electrodes decorated by the samples were activated in the potential range of -1.5 to 0.5 V for 20 cycles. The results of CV from the activated electrodes are shown in Fig. 7. According to Fig. 7, A sharp peak (C) at -1.04 V was attributed to water decomposition and hydrogen adsorption in the cathodic direction. While appeared peak (A) at -0.69 V was ascribed to hydrogen desorption in the anodic direction. According to Fig. 7, two sharp peaks were exhibited at -1.04 V and -0.69 V, in cathodic direction (C) was attributed to water decomposition and hydrogen adsorption and in anodic direction (A) was ascribed to hydrogen desorption. It is worth to mention that the CV of bentonite demonstrates low current for C and A peaks, to put it differently bentonite can adsorb/desorb a small amount of hydrogen due to its high surface area. Comparing CV profile of bentonite and B-T shows a significant increasing of the current of C and A, this could be described by two aspects: adding TiO₂ led to increase surface area and create negative charged centers which are beneficial for hydrogen adsorption, and the second one is that TiO₂ decoration eventuated to raise more oxygen groups which are reduced with ease [106]. According to Fig. 7, the second anodic peak (B) at ~0.2 V, indicates the oxidation of the hydrogen atoms by releasing hydrogen ion to form water by combining OH⁻[14, 106]. Furthermore, the results obtained from Fig. 7 indicate an increase in the anodic current due to the addition of Au NPs. Au NPs increase the hydrogen storage capacity owing to improved porosity and conductivity; it is worth to note that hydrogen spillover process through Au NPs may be contribute to facilitate hydrogen adsorption on the surface of electrodes. The influence of Au NPs' content on hydrogen storage was assessed by comparing the current of A. Increasing current was observed by increasing Au NPs from B-T/Au-6 to B-T/Au-12, in contrast it was declined for B-T/Au-18. The aforementioned reasons concluded that presence of TiO₂ and Au NPs play a vital role in hydrogen storage; admittedly, it must be mentioned extra-loaded NPs could block host active sites, consequently less active positions may remain to absorb the reduced hydrogen atoms.

In order to investigate and compare different samples in terms of hydrogen adsorption/desorption, the current of reduction and oxidation peaks, I_C and I_A, are listed in Table

Commented [B1]: The CV of activation process for all electrodes are shown in Fig. 7.

3. Therefore, the results of the activated electrodes show that B-T/Au-12 has a better hydrogen adsorption and desorption compared with the other samples after 20 cycles.

To investigate the influence of potential windows on hydrogen storage capacity, the CV test was applied for B-T/Au-12 under the same conditions but in -1.5 to 0 V and the CV profile is depicted in Fig. 8. To get rid of any suspicion, the CV was tested for pure mesh substrate; according to the CV pattern obtained for the mesh substrate (see Fig. 8a), there are no redox peaks in the potential window of -1.5 to 0 V; i.e. there is no hydrogen adsorption and desorption. According to Fig. 8b, when the potential becomes negative enough, the cathodic current starts and it increases to the reduction peak (C) at -1.04 V. Afterwards, the formation of hydrogen atoms was occurred in the alkaline solution and it was adsorbed on the surface of B-T/Au-12 electrode. The reduction peak in cathodic direction shows the charging process due to the electrical polarization [86, 87]. The scan direct was switched to positive at -1.5 V for scan back and the anodic current was started when the electrode became strong oxide. Next, the anodic current increases to the oxidation peak (A) at -0.69 V. In the oxidation peak, hydrogen atoms are released from the working electrode surface. Finally, when the potential reaches its initial value (0 V), the scan completes. The CV of B-T/Au-12 shows by eliminating the second anodic peak (B), located at 0.2 V, the height of C and A is declined by time passing. As shown in Fig. 8c, in the first 48 cycles fast decay has occurred due to electrode oxidation [86] and the current has been constant at $\sim 0.46 \text{ Ag}^{-1}$ after 150 cycles. Consequently, to get better conditions the B-T/Au-12 was activated in -1.5 to 0.5 V and optimum condition was obtained by cycling test.

The mechanism of hydrogen adsorption and desorption was performed in accordance with following chemical reaction.

The water decomposition and hydrogen adsorption was occurred at -1.04 V involving Volmer reaction (6).



Then, these adsorbed hydrogen atoms were desorbed due to Tafel reaction (7) or Heyrovsky reaction (8) and strong peak was observed at -0.69 V.





The peak located at 0.2 V exhibits oxidation of adsorbed hydrogen atoms through following reaction:



These process could be reversible because through equation 10 water is one of the end product.



Subsequently, B-T/Au-12 was optimized in 190 cycles in the potential window of -1.5 to 0.5 V to improve hydrogen production and storage capacity, and the CV data for optimization process is shown in Fig. 9. Comparison CV elucidates increasing the current of C and A by time passing and this is could be justified by creating new host active site [102, 107, 108]. The current was steadily increased from the first cycle to 169th cycle, and it is almost constant until a sharp decline was taken place at 176th cycle and it is probably down to electrode damaging or oxidation.

Accordingly, the maximum hydrogen storage capacity of B-T/Au-12 was obtained from 176th cycle. The optimum cycling was achieved after 190 cycle, the optimization is stopped and the adsorption and desorption of hydrogen through B-T/Au-12 was investigated. In order to investigate the hydrogen storage ability of B-T/Au-12 electrode, the potential window was changed and CV measurement was performed in the range of -1.5 to 0 V at 100 mVs⁻¹ sweep rate. Fig. 10 shows the CV curve of adsorption and desorption hydrogen for activated B-T/Au-12 electrode and the current becomes constant in ~3 Ag⁻¹ after 150 cycles.

The amount of hydrogen stored on the working electrode surface in the charging process can be obtained by integration of the oxidation peak. The double layer and faradic reaction occur when the equilibrium potential is lower than the applied potential. Therefore, the part of double layer should be separated from the oxidation peak to measure the amount of adsorbed hydrogen. The pink area in Fig. 11a corresponds to the double layer while the other part of the oxidation peak shows the amount of the stored hydrogen. Therefore, integration is found using the formula below:

$$Q_H = \frac{1}{9} \int_{-0.9}^{-0.1} (I_a - I_{dl}) dE \quad (96)$$

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where ϑ is the sweep rate, I_a and I_{dl} are the currents due to the anodic peak and double layer charging, respectively, and dE is the potential window [109].

Fig. 11b and c are associated with the investigation of the cyclic life performance during 250 cycles before and after activation. In this Figure, Q_H is obtained from Eq. 26 and has been plotted as a function of the number of cycles. According to Fig. 11b, in the first 48 cycles, fast hydrogen storage capacity decay is observed due to the oxidation of electrode surface [86] and the amount of hydrogen charge decreases to constant value of $\sim 3 \text{ Cg}^{-1}$ after 150th cycle. Fig. 11c shows the amount of hydrogen charge of activated electrode; the hydrogen charge reaches constant value of $\sim 15 \text{ Cg}^{-1}$ for the last 100 cycles after fast decay. Accordingly, the activation process can be used for increasing hydrogen storage capacity.

SEM assay was used in order to study changes on the surface of the B-T/Au-12 after the CV process. Throughout SEM pictures, the presence of nanocomposite on the surface of mesh was confirmed, and lamellar structure was noticed for nanocomposites. Comparison of Fig. 12c and f suggests that the surface was slightly smoother and the crystals of KOH can be observed on the surface of nanocomposite after electrochemical test. The decrease of hydrogen storage can be described by two aspects: decreasing roughness and blocking active host sites. As other reports documented, roughness and pores contribute to adsorption hydrogen; therefore, being smoother and blocking some pore probably led to decreasing hydrogen adsorption.

Comparison reported hydrogen evolution of TiO₂-based nanocomposites with B-T/Au-12 nanocomposite in related to current research, is summarized in Table 4.

4. Conclusion

Various ablation times were used in the synthesis of Au NPs with the size range of 20-58 nm by LAL process, which were then successfully loaded on B-T nanocomposite by facile stirring method. The hydrogen storage capacity of the nanocomposites prepared was tested by CV in alkaline medium. The results obtained demonstrate that the decorated electrode *via* B-T/Au-12 has the highest hydrogen storage capacity, which is about 15 Cg^{-1} . The results obtained show that the

presence of Au NPs can improve the hydrogen storage owing to their hydrogen spillover, improved porosity.