Experimental and Theoretical Investigation of Glucose – Graphene Hybrid for Increasing the Natural Gas Storage

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ABSTRACT: *Several categories are usual ways for natural gas storage: Compressed Natural Gas (CNG), Adsorbed Natural Gas (ANG), and liquefied gas methods. The ANG technologies allow natural gases to be absorbed via porous materials at high temperatures and low pressures, around 500 psig (3.5 MPa). Via an accurate comparison, it has been exhibited those gases can be stored in a CNG tank at approximately 3,500 psig. Therefore, the ANG system appears to be prospective for any future activities. In this study, Glucose–Graphene hybrid based materials with hierarchical structures, tunable surfaces, chemical doping, and functionalization were simulated for gases with $\gamma = 1.41$ such as (H_2, N_2, O_2) and $\gamma = 1/33$ for (CH_4, CO_2, NH_3, NO_2, H_2S, SO_2) and $\gamma = 1.67$ for (He, Ne) sorption, storage, and separation. The scope of this work is to produce a new Nano-adsorbent, i.e., Hybrid -Glucose-Graphene, which can be introduced as a new candidate for that gas storage.*

KEYWORDS: *Adsorbed gas; ASAP; Storage test, Glucose, Graphene oxide; G-As-Pt, doping.*

INTRODUCTION

Native gases have been used as a crucial pure fuel in past decades before H_2 fuels that commercially were available in many places. Besides, Methane and Ethan have also been known as renewable clean energy sources [1, 2]. Three different types of methods are general for storing natural gas: the liquefied form of gases (LNG), compressed form of gases (CNG), and adsorbed form of gases (ANG). In the LNG system, cost, requirement for insulated vessels, and the flammability nature of it may seem to be an unsuitable method. Nevertheless, in contrast, LNG and CNG system has been commercialized in the whole world as a suitable and economical method. However, there are several problems associated with it is due to their high-performing pressures. In the ANG system, natural gases can be saved in porous materials or adsorbents and act at low pressure at room temperature. However, one of the main problems in the ANG processes is the evaluation of adsorbents [(2, 3]). The efficiency of Activated Carbon's (AC) properties is closely connected to the adsorbent systems within a range of pore size distribution [3, 4]. It is traditionally approved that the methane adsorption on activated carbon is by van der Waals forces [4-6].

Obviously, due to the porosity of the CH_4 surface, for better adsorption properties, the effort must be put into the preparation of activated carbon with a large surface area to maximize the adsorption capacities [2, 3].

Suitable adsorbents must have highly microporous surfaces with high packing densities. Therefore CH_4 adsorption capacity efficiency can be measured with volumes of adsorbed natural gas and also measured at standard conditions or per storage volume (v/v). The highest index of these capacities has been obtained at 3.5 MPa, and 25 ℃, which is for the high efficiency activated carbon [5-8]. Various studies have considered the synthesis of activated carbon with high specific surfaces and high volumetric capacities through using agricultural waste materials, such as coconut, walnut, cherry stones, olive, and peach stones, that contain high carbon [6].

Glucose and sucrose are the most general carbohydrates as mono or disaccharides. Synthesize of Glucose *via* chlorophyll in plants by using CO_2 from the air and sunlight as the energetic catalyst sources are firstly accomplished applying. Glucose appears in various molecular structures and is stereochemistry in a conformational situation. However, all of these combinations can be separated into two groups of mirror images. Only one set of those isomers exists in the natural product obtained from the right-handed form" of glucose (D-glucose) [9-12]. Carbon is an exciting element in the periodic table, and graphene is a two-dimensional form that, in the past decade, has received significant attention. It has an unusual or non-equal character in nature. Graphene is a 2-D honeycomb sheet of sp^2 hybridized with unique properties. These structures of carbon atoms can make a complicated network as a strong foundation inorganic chemistry. Even elemental carbons show a tough role, forming several very different combinations [12].

By investigating through modeling and simulation of graphene hybrid and graphene oxide (Fig. 1), non-enzymatic detection might be reached through the adsorption of glucose on the surface of graphene or GO sheets. In the GO surface, the OH- groups of glucose can link to O_2 on the graphene oxide sheets. These results are in agreement with *Abdullahi et al*. [1] studies. Glucose sensing is related to the glucose oxidation by air on the GO layers and noble metals (Palladium, Platinum, Rhodium, and Titanium) as a catalyst, then decomposition into lactone and H_2O_2. This molecule passes through the
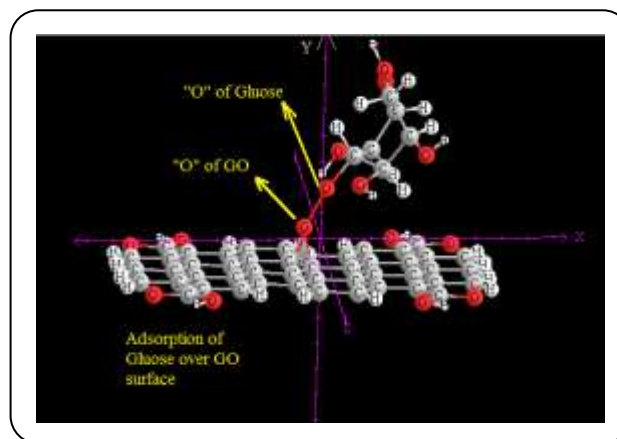

Fig. 1: Adsorption of glucose molecules on the Graphene Oxide (GO) surfaces (optimized structure).

structure of the graphene layers' porous and, consequently, changes to O_2 gas, H+ ions, and electrons.

The oxidation details accomplish in air, under several controlled temperatures. So, the detection in the suggested devices is non-enzymatic with high feasibility and variability plus minor sensibility [13-15]. By using adsorbents in the storage, the sizes can be lessened without deserting the quantity of the natural gases while reducing the pressure inside the storage vessel [16-19]. The ANG method causes the natural gas to be absorbed *via* a porous adsorbent material at low pressures, around 550 psig. Compared to Natural Gas-powered Vehicles (NGV), this gas can be stored in a CNG tank at approximately 25 MPa [16, 17]).

Therefore ANG techniques that save CH_4 by adsorption on micro carbonaceous adsorbents at medium pressure and room temperature appear to be prospective. The scope of this work is the production of a new Nano-adsorbent on a laboratory scale. This Nano adsorbent can be introduced as a new candidate for natural gas storage. Purified Glucose-Graphene Hybrid synthesized by the oven method was used as an adsorbent for methane adsorption studies.

THEORETICAL SECTION

It was confirmed that Nobel metals (Palladium, Platinum, Rhodium, and Titanium) produce electro-catalytic activities in H_2O_2 redox reactions [16]. In this work, we simulated and doped these metals on the graphene surface. The advantages of noble metals such as platinum thin films accumulated using Atomic Layer

Deposition (ALD) over thickness (40-45) nm via using Chemical vapor deposition [17, 18].

Glucose oxidation on the layer of GO, yields H_2O_2 molecules that pass through the porous GO thin films and consequently can be adsorbed on the Pt with physical kinetics adsorption.

During the electrochemical oxidization on the sheet of platinum electrodes, the following reaction occurs [19]

$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$
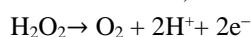
Nobel metals such as Pt Nanoparticles are the primary elements for the redox of H_2O_2 and the concentration of this molecule modified with the concentration of the glucose solution. The advantage of this kind of sensors is the vast area that is provided through the graphene with Pt-doped nanoparticles.

This ample space heightens the reaction's speed and increases the yield of the oxidation of H_2O_2 molecules. Electrochemical activities can be investigated via Cyclic Voltammetry methods and ampere-metric approaches. The other profit is the balance of relevant devices after each test. The sensitivity of the devices increased by enhancing the porous structure of graphene which gives the potential of H_2O_2 molecules to confine and concentrate [18-20].

Mechanism of sensor

The modeling is related to the cooperation of γ–photons with the graphene sheets, which changes the distribution of local electrical fields. In the structure of the glucose-sensing and spinning voltages are used an n-type Si in which the performance power of platinum (i.e., 5.99 eV) is higher than that of the Silicon (4.55 eV). Therefore capabilities are decreased. The current across the platinum/n/silicone junction is appeared due to basic carriers. As mentioned, there are a few ways by which current might flow, including emission, diffusion, thermionic, and tunneling effect (Fig. 2).

In this investigation, 3-D structures of Glucose-Go/graphene-based Pt-As (GO/G-Pt-As) (Fig. 2) were modeled using gas adsorption. Graphene Oxide (GO) and glucose was used as a matrix and a frame, respectively, for the GO's situation in several dielectric communications. G/GAs exhibit compact mesoporous size spreading, high surface area, and hierarchical mesoporous structures.

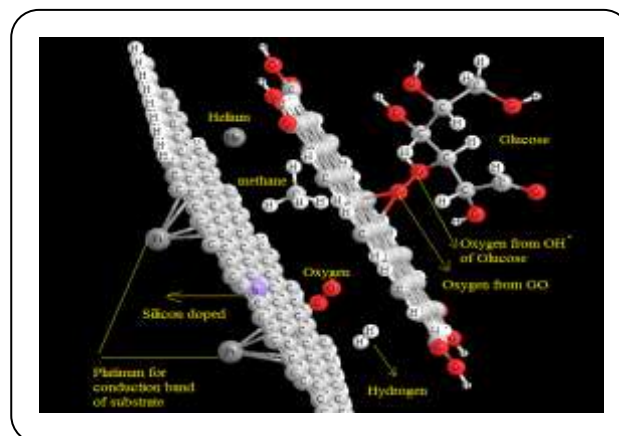These features presented G/GAs being suitable adsorbents for H_2, O_2, CH_4, and He (Fig.2). Glucose-

Fig. 2: Theoretical investigation of Glucose–Graphene Hybrid as an adsorbent for O_2, H_2, He, and CH_4 gases.

Go/graphene-based Pt-As (GO/G-Pt-As) is a type of 3D network structure, which is calculated via the overlapping of graphene sheets [21]. It is utilized in different fields such as adsorption, catalysis, and energy-saving, due to its magnificent surfaces and physical properties they have. As compared to other activities, the hydrothermal systems rely on the self-multitude of graphene beyond reactants adding [20]. These kinds of methods can keep the essential properties of GO and retain them while producing GO/G-Pt-As. However, GO hydrogels are straightly provided through hydrothermal reduction [21].

Along with hydrothermal reduction, practical molecules can form a few numbers of free oxygen, and so, the produced gases cannot follow the best characteristics of graphene completely. During the forming process, adding a binder material to GO, can solve this problem. In Recent research, during GA preparation, synthetic polymers, such as propylene carbonate, p-phenyl-diamine, and poly-ethylene-amine, were used as binder materials to crosslink [22].

EXPERIMENTAL SECTION

Processing the sample includes Nano activated carbon samples from GO and glucose, followed by a general procedure. Glucose powders were sieved to obtain a particle size between 0.5 mm to 1 mm and mixed with a specified amount of GO solution prepared by the Research Institute of Petroleum Industries (RIPI) of IRAN. Glucose/GO mass ratios of 1:1, 2:1, 1:2, and 5:1 were employed in this study. Then the samples were mixed and homogenized in ultrasonic at room temperature.
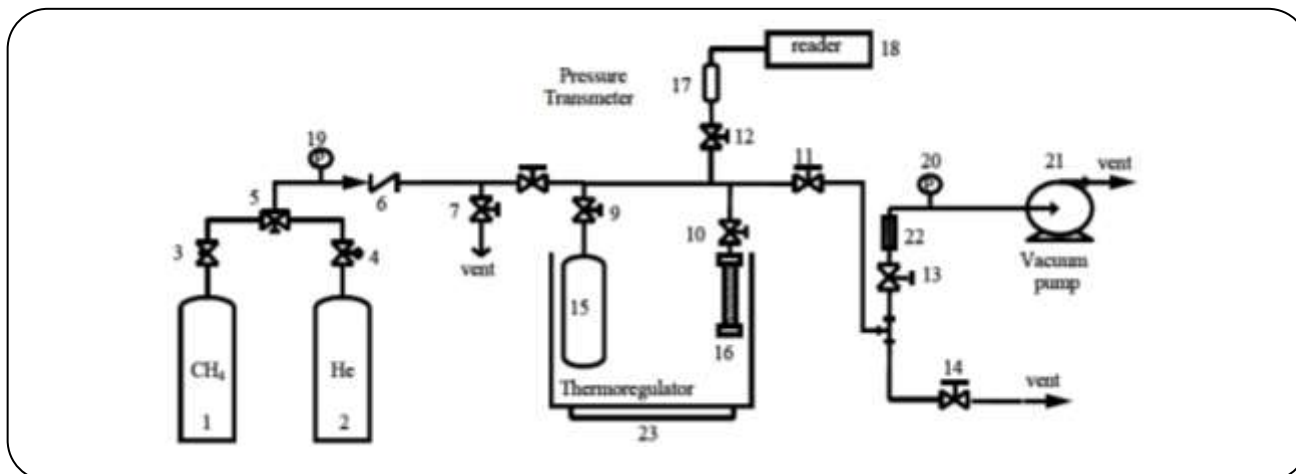
Fig. 3: Experimental apparatus: (3, 4) regulators, (5) three-way valve, (19, 20) pressure gauges, (6) check valve, (7-14) valves, (15) reference vessel, (16) adsorption vessel, (17) pressure transducer, (18) reader, (21) vacuum pump, (22) filter.

Subsequently, the samples were placed in an oven. The temperature of the oven was set at 800 °C at a rate of 12 °C/min, which was retained for one hour under nitrogen flow. Samples were labeled and analyzed for the BET area, total pore volume, microspores volume, and methane storage test.

Determination of volumetric helium (dead volume)

In this research, an investigation of methane adsorption on nano-activated carbon was used by the volumetric method. The diagram, which is shown in Fig. 3, reveals the technicalities of the equipment used to perform the experiments. It is essential to calculate the dead volume comprising macro-pores and mesoporous for the adsorbent, and the void faction inside the adsorption cell to determine the amount of natural gas adsorbed on the Nano activated carbon. It should be released that gas adsorption does not happen within the dead volume of the adsorption cell. In the first stage of this test, the Nano activated carbon sample was degassed in a vacuum oven at 200 °C temperature for 2 hours. In the next step, the adsorption cell was plugged up with the degassed adsorbent. The dead volume inside the cell was arranged for helium injection from the reference cell, which was filled with helium gas until the initial pressure was in advance, and the adsorption cell reached the thermodynamic equilibrium condition by opening the associating valve. The total volume of the reference and adsorption cells was adopted to be V_2, where helium could penetrate V_2 could be calculated using P_1 as the initial pressure of

the reference cell, P_2 being the equilibrium pressure of the whole system and V_1 was the volume of the reference cell volume (21)

Hence, for determining the dead volume (V_{void}) inside the adsorption cell, the following relation was employed:

$$V_{void} = V_2 - V_1 \qquad (1)$$

Determination of the natural gas adsorption (Methane)

The sample inside the adsorption cell is degassed under vacuum terms, then the methane injection is executed. For methane injection, at the first stage at a fixed pressure, the reference cell is filled with methane. By opening the connecting valve, the gas from the reference cell is injected into the adsorption cell. After reaching equilibrium, the connecting valve between the adsorption and reference cells was closed [2].

By the following method, the methane adsorption would be measured:

$$P_1V = Z_1n_1RT \qquad (2)$$

$$P_2V = Z_2n_2RT \qquad (3)$$

In these equations, P_1 and is the initial pressure of the reference cell, and P_2 is the equilibrium pressure of the adsorption, and V is the volume of the reference cell. Also, n_1 and n_2 revealed the numbers of methane's mole before and after equilibrium in the reference cell. Z_1 and Z_2 are the compressibility factors of methane in the reference cell before and after equilibrium. The amount of methane captured in the dead volume of the adsorption cell can be determined by:

Table 1: Packing density, BET surface area values for the adsorbent prepared in our laboratory.

Sample	A_s BET (m^2/g)	pore volume (cm^3/g)	V_p (cm^3/g)	A_p (m^2/g)
Glucose + Graphene (1:1)	1.4600E+02	8.6659E-02	3.5351E-02	17.719
Glucose + Graphene (1:2)	1.3900E+02	8.5667E-02	3.2357E-02	17.534
Glucose + Graphene (2:1)	1.5276E+02	8.7657E-02	3.8653E-02	17.918
Glucose + Graphene (5:1)	1.7345E+02	9.2328E-02	4.1202E-02	18.198

$$n_{void} = \frac{P_{void} \, V_{void}}{ZRT} \qquad (4)$$

Where, n_{void}, P_{void}, and V_{void} are the mole numbers of methane captured in the dead volume of the adsorption cell, the equilibrium pressure of the adsorption cell, and the dead volume of the adsorption cell, respectively.

Adsorbent characterization

Brunauer-Emmett-Teller (BET) surface area analysis and t-plot micro-pore volumes were calculated based on the nitrogen adsorption isotherms measured with a volumetric adsorption apparatus (Micro ASAP2400).

RESULTS AND DISCUSSION

The prepared Nano adsorbent was characterized by BET, BJH, and methane storage analysis. The surface area and packing density of Nano adsorbent are presented comparatively in Table 1. As shown in Table 1, the addition of glucose to graphene greatly enhanced the BET surface area and volume micro-pores of samples. The sample with the ratio of (glucose + graphene (5:1)) had a higher surface area than other samples. It seems that the destruction of glucose to carbon at 800°C modified the Nano-structures characteristic of graphene. The glucose had changed to carbon at high temperatures; moreover, glucose had a direct impact on the nanostructure of sample pores, which are essential in methane storage capacity. Nanoparticles, as an efficient adsorbent with a large specific surface area, have been recognized by a hybrid of glucose and graphene. The methane storage capacities of samples are presented in Fig. 4. The result revealed that the amount of CH4 adsorbed at 35 bar (3.5 MPa) is related to the mass ratio of glucose and graphene. It can be discovered that by adding glucose to graphene, the methane adsorption capacity increased. The results also show that the amount of methane adsorbed in the Nano adsorbent is different according to the percentage of glucose added to graphene. As shown in Fig. 4, the total volume of methane adsorbed was enhanced by increasing glucose. This finding is in agreement with the higher development of porosity obtained with CH$_4$ (Table 1).

It should be noted that for samples with high glucose content, exceptional values of methane uptake were obtained. Also, Fig. 4 included that the destruction of glucose to carbon had a significant effect on the improvement of the adsorbed methane capacity of graphene. The hybrid of Glucose and Graphene showed significant behavior and characterization in methane storage.

In the research, various parallels have been proposed between methane adsorption at 298 K and porosity parameters collected from N$_2$ adsorption at 77 K (20, 22). In the latest analysis, the plot of methane adsorption capacity versus surface area or micro-pore volume obtained from N$_2$ adsorption at 77 K is ruined for those that have narrow micro-porosity. In another work, with the total microspore volume (both the fine microporosity and super microporosity), the best interaction was achieved between methane storage capacity and porosity at 273 K [2, 20].

CONCLUSIONS

In this study, the hybrid of graphene and glucose was studied for methane storage applications. The Adsorbed Natural Gas (ANG) method can potentially reduce the highest storage pressure so that these Nano Activated Carbons are recognized to be very suitable adsorbents for methane storage, due to their high microporous potential. In this paper, the behavior in methane storage of Nano adsorbents at different pressures has been presented. Nano adsorbents with a high methane uptake and a high surface area can be produced from glucose. The comparison of the different pressures have enabled ANG to be commensurate with compressed natural gas CNG. By adding glucose to graphene, the stored methane capacity increased beside the percentage of glucose has a significant impact on
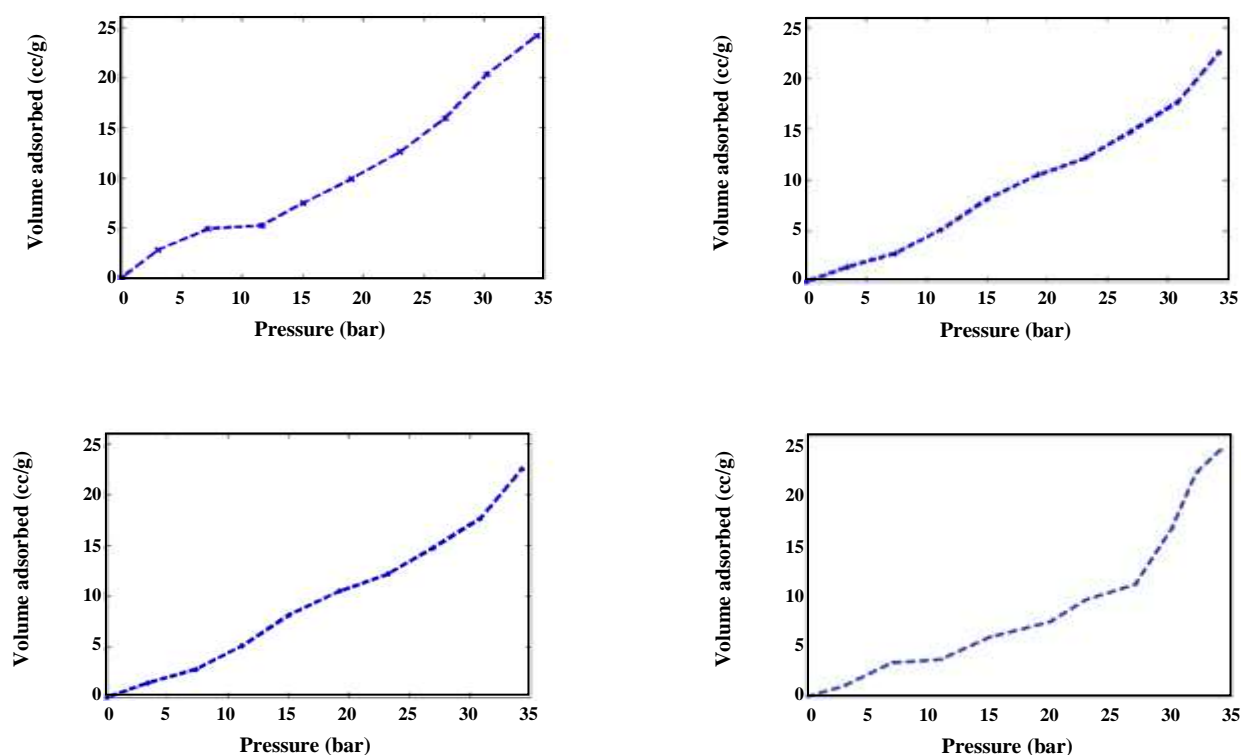
Fig. 4: Adsorption isotherms of CH4 on adsorbent at 295K up to 35 bars: A: Glucose + Graphene (1:1),
B: Glucose + Graphene (1:2), C: Glucose + Graphene (2:1), D: Glucose + Graphene (5:1).

methane storage. The sample with the ratio (Glucose + Graphene (5:1)) presents a suitable adsorbent for methane storage, due to the excellent characteristic of glucose which has changed to carbon at a high temperature 800°C and improves the GO nature.

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