The effect of molecular dynamic energy of photocatalysts on hydrogen production

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Abstract. Activated Carbon (AC) and Clitoria Ternatea Powder (CTP) were used as photocatalysts to produce hydrogen gas from water. Photocatalysts were characterized by SEM-EDX and FTIR. Photocatalysis was carried out for 1 hour using 300 W halogen blue light. The resulting gas was measured in ppm using the MQ 8 gas detector and converted into μmol. In photocatalysis, the various ratios of AC and CTP affect the molecular dynamic energy. The molecular dynamics energy was estimated with Hyperchem software. At the case of constant AC while increasing the number of CTP, the molecular dynamics energy increases from 524,143 kcal/mol to 801,488 kcal/mol. Whereas in the case of constant CTP while increasing the number of AC, the molecular dynamics energy only slightly increase from 524,143 kcal mol⁻¹ to 541,527 kcal mol⁻¹. Molecular dynamic energy in both cases is directly proportional to the hydrogen gas production in the first case, increasing CTP the hydrogen production reaches 2635 µmol g⁻¹ h⁻¹. Whereas in the second case, increasing AC, the hydrogen production tends to be constant. These results indicate the AC will play an optimal role as catalyst support when most of its defects are filled with CTP the defective grapheme in AC boosts the behaviour of electrons in the aromatic ring of CTP. In the future, it will be a step forward for the production of hydrogen gas in an environmentally friendly way.

Keywords: activated carbon, clitoria ternatea powder, photocatalyst, molecular dynamic energy, hydrogen

1. Introduction
Hydrogen is a green fuel, emission-free and inflammable fuel. Due to this advantage, hydrogen has been used to substitute fossil fuel as an alternative fuel [1]. Hydrogen has been generated from different energy sources such as renewable and non-renewable fuels, especially steam reform of methane.

There are various hydrogen manufacturing processes such as steam reforming. Thermochemically, hydrogen is generated in high-temperature (700 °C to 850 °C) chemical reactors by processing hydrocarbons (such as oil, coal, biomass or waste) in the form of a synthetic gas comprising H₂, CO, C₂, H₂O, and CH₄. However, this approach is high costs, including higher heating, processing of hydrogen and storage costs [2]. Second method is electrolysis. Electrolysis is less expensive than steam reforms in terms of costs. Nevertheless, hydrogen efficiency is very low due to high energy consumption and low development rates of hydrogen through water electrolysis [3-5]. The third way is the water-splitting photocatalysis. As it is made from an abundance of raw material and as the reaction products are harmless, the water-splitting reaction...
at room temperatures is a promising option [6]. This water-splitting reaction involves some basic processes initiated through the absorption of solar radiation that enable the promotion of a valence band electron to drive an electron-hole pair. These pairs play key roles in the redox processes that take place during the water-splitting reaction. Electrons are known to reduce protons to hydrogen molecules, while anion oxygen is oxidized through the hole. Due to the level of water oxidation, the conductive band should be more negative than the valence band [7].

Photocatalysts that have been developed are metal-carbon composites and bio photocatalyst. Metal-carbon composites such as carbon nano tube film (CNTF) with CuS-ZnS, Leading CNT films can prevent the recombination of electron-hole photogenerated pairs. The deposition of CuS nanoparticles on the ZnS / CNTF results in greater photocatalysts which can be due to the successful separation of the electron-holes. The porous structure helped to establish effective contact between the sacrificial agent and photocatalysts, resulting in increased production activity of H₂[8].

Under visible light irradiation, the atomic intersection promotes rapid transfer of an electron from nanofibers to MoSe₂ to reduce rapid recombination kinetics in WO₃ nanodots and extend the life of the charger WO₃ and release more photogenerated electrons with higher power reductions for the production of the hydrogen [9]. The floral graph (FG) can help to absorb light, adsorb slaughterers in the solution and separate photogenerated carriers. The FG-ZnS nano composites show the enhanced activity of the production of photocatalytic hydrogen in comparison with pristine ZnS photocatalyst [8].

The improved photocatalytic hydrogen output is due to the synergistic impact between the conductive carbon layer and the CoP surface cocatalyst, with the result that photo-excited carriers are efficiently separated and abundant hydrogen active sites are reduced [10]. The tendency of nanofibers polyacrylonitrile (PAN) has been used to assemble in an integrated flexible mat through electrospinning. This mat has the same flat and elastic nature as a leaf and has a hierarchically porous structure which can have a similar function to stomata. These special features make PAN mat a high performance, organized leaf-like composite photocatalyst with ideal flexible substrates [11]. This system consists of a two-step reaction: (1) the reduction of TiO₂ methyl viologen (MV) and hydrogen synthesis with reduced MV using biocatalysts. Good material for clean hydrogen production is biocatalysts [12].

There are still drawbacks to the previous study of photocatalysis. The process was complex and not comparable to the emitted hydrogen. A simplified method for processing gas in large quantities is therefore required. In this study, AC and CTP have been used as photocatalysts to breakdown the water molecules. AC was made from coconut shells consisting of defective graphene sheets. Graphene is monolayered in two-dimensional layers of sp² hybridized carbon atoms arranged in honeycomb grids with its outstanding electronic, thermal, optical and mechanical properties [13].

Defective graphene can repair itself with attracting carbon atom from the hydrocarbon compound. We were used CTP as a hydrocarbon compound. CTP was made from the Clitoria Ternatea flower. They are bright blue or white and are relatively large, and are therefore used worldwide as a decorative element. Due to its high durability, the blue flower pigment in Southeast Asia is usually used as a food colorant. Blue anthocyanins in petals of CT are the terminations. These are delphinidin-based acylated anthocyanins [14].

AC and CTP play a key role in water decomposition. The main components of AC and CTP are aromatized carbon rings. As AC and CTP gain energy from light photons, the electron delocalization is more energetic and the electrons spin more rapidly triggering AC and CTP magnetic fields. This magnetic field causes water molecule decomposing into oxygen and hydrogen gases gradually.
2. Method
The experimental apparatus installation is shown in Figure 1. The production of hydrogen was performed in a closed-gas circulation system with a total volume of 700 mL. Various quantities of bio photo catalyst elements in the form of AC and CTP with a composition of 5 mg, 10 mg, 15 mg, and 20 mg respectively were dispersed in 350 mL distilled water. 300 W halogen blue light was used for the photo reaction. The hydrogen production was measured using the MQ-8 hydrogen gas sensor. The hydrogen gas production can be recorded into computer memory using Arduino Uno Software. MQ-8 hydrogen gas sensor was placed in a transparent glass tube hydrogen gas collector. The hydrogen production recorded in ppm by the MQ-8 sensor was converted into µmol g⁻¹ h⁻¹.

2.1 Characterization
The functional groups were analyzed by IR Prestige 21, Fourier transformation infrared (Shimadzu, Japan). The morphological features of the samples were observed by inspect-S50, scanning electron microscope (FEI, USA).

2.2 Photocatalysis
The production of hydrogen was performed in a closed-gas circulation system with a total volume of 700 mL. Various quantities of photocatalyst elements was dispersed in 350 mL water. The 300 W halogen blue light was used for the reaction. The cell's photoreaction temperature was approximately 70°C. The generated hydrogen was analyzed using the MQ-8 sensor with a high purity hydrogen calibration curve (Air Liquid 99.99%) acquired before measuring. For activity measurements, light irradiation time was 1 hour.

3. Result and discussion
3.1 SEM
The characterization results are shown in Figure 2. It can be seen from SEM image that AC contains pores around 75 nm whereas the CTP has shape like flakes.
Figure 2. SEM Image: (a) AC and (b) CTP

3.2 EDX

Figure 3 shows that AC consists of 87.12% oxygen; 9.5% oxygen; 0.73% silica; and 2.66% potassium.
Figure 4 shows that CTP consists of 40.52% carbon; 47.22% oxygen; 5.27% magnesium; 5.19% potassium; and 1.8% calcium.

3.3 FTIR

Figure 5 indicates FTIR results of AC and CTP. The appearance of a peak in the wavenumber 2850-2970 cm$^{-1}$ indicates the presence of the C-H Alkane group. The appearance of a peak at the wavenumber 3200-3600 cm$^{-1}$ indicates the presence of an O-H group of hydrogen/phenol bonding alcohols.
3.4 Molecular dynamic energy of photocatalyst

Table 1. Molecular dynamic energy of activated carbon

| Molecule             | Molecular Dynamic Energy (kcal/mol) |
|----------------------|-------------------------------------|
| Graphene no defect   | 408.721                             |
| Graphene 1 defect    | 412.392                             |
| Graphene 2 defect    | 414.488                             |
| Graphene 3 defect    | 418.7                               |
| Graphene 4 defect    | 423.386                             |
Table 2. Molecular Dynamic Energy of Clitoria Ternatea Powder

| Molecule | Molecular Dynamic Energy (kcal/mol) |
|----------|-----------------------------------|
| 1 CTP    | 85.047                            |
| 2 CTP    | 166.936                           |
| 3 CTP    | 244.594                           |
| 4 CTP    | 323.525                           |

Tables 1 and 2 show molecular dynamic energy in AC and CTP. AC consists of defective graphene. The AC of 5 mg, 10 mg, 15 mg, and 20 mg are estimated with 1, 2, 3, and 4 defects respectively. Whereas CTP of 5 mg, 10 mg, 15 mg, and 20 mg are estimated with 1, 2, 3, and 4 molecules of CTP respectively. Increasing the amount of defective graphene increases molecular dynamic energy. Molecular dynamic energy is shown to be directly proportional to the kinetic energy of a molecule. An increase in molecular dynamic energy indicates the increase of electron motion energy that easier to dissociate the bonds of water molecules.
Table 3. Molecular Dynamic Energy of AC Constant + Various amount of CTP + Water

| Molecule            | Molecular Dynamic Energy (kcal/mol) |
|---------------------|-------------------------------------|
| AC 5mg + CTP 5mg    | 524.143                             |
| AC 5mg + CTP 10mg   | 635.251                             |
| AC 5mg + CTP 15mg   | 717.863                             |
| AC 5mg + CTP 20mg   | 801.488                             |
Table 4. Molecular Dynamic Energy of CTP Constant + Various amount of AC + Water

| Molecule          | Molecular Dynamic Energy (kcal/mol) |
|-------------------|-------------------------------------|
| AC 5mg + CTP 5mg   | 524.143                             |
| AC 10mg + CTP 5mg  | 528.447                             |
| AC 15mg + CTP 5mg  | 541.183                             |
| AC 20mg + CTP 5mg  | 541.527                             |
3.5 *Hydrogen production by photocatalysis method*

Photocatalysis begins with the transfer of energy from light to the AC and CTP photocatalysts. This energy makes the photocatalyst electrons delocalized. AC consists of defective graphene. Due to the defect, the electron delocalization in defective graphene becomes more energetic than that in the aromatic carbon ring. On the other hand, CTP has a hydroxyl functional group. Electron delocalization in defective graphene has a role in increasing the electron delocalization of the hydroxyl functional group in CTP strengthening its magnetic fields to disrupt and break the bonds of water molecules. The experimental data have been found to prove the effectiveness of the ratio of photocatalysts on hydrogen production as shown in Figure 6 and 7. In the case of increasing the number of CTPs from 5 mg to 20 mg while keeping the AC constant at 5 mg the hydrogen production increases from 800 to 2600 µmol g\(^{-1}\) h\(^{-1}\) nearly 3.2x. This result is directly proportional to the molecular dynamic energy produced (see Table 3). This indicates that the only 1 defective
graphene could boost the delocalized electron in the increased number of CTP since presence of hydroxyl functional groups in CTP whose dipole moment is also strengthened by AC attracts electrons to transit at OH groups. This makes electrons move more actively and produces stronger magnetic fields to disturb water molecules. Water molecules consist of hydrogen bonds and covalent bonds. At first, the electrons will weaken the hydrogen bond. When the hydrogen bond has weakened, the effect of the magnetic field of other hydroxyl functional groups breaks the covalent bonds in water. So hydrogen gas can be produced. Then in the second case, the number of AC was increased from 5 mg to 20 mg keeping constant the CTP. The hydrogen production tends to be constant in the range of 800 μmol g⁻¹ h⁻¹ - 1100 μmol g⁻¹ h⁻¹. This shows that the increase in the amount of AC is not too significant to increase the rate of hydrogen production. This condition is directly proportional to the molecular energy dynamic in Table 4, which is in the range 524 kcal/mol - 541 kcal/mol. This suggests that the defect in AC is only good as catalyst support for CTP. In order to get most powerful photocatalyst, most of the defects should be filled with CTP. In previous studies, Zha used Cds, Pt, Coconut shell carbon nanosheets (CSC) photocatalysts which produced 1679.5 μmol g⁻¹ h⁻¹ [15]. Xiang used photocatalyst Cds, WS2, graphene with hydrogen gas 1842 μmol g⁻¹ h⁻¹ [16]. In this study, the hydrogen produced reached 2635 μmol g⁻¹ h⁻¹. When compared with other studies our research can produce higher hydrogen production.

4. Conclusions
The increasing molecular dynamic energy of photocatalytic AC and CTP is proportional to the increase in hydrogen production. AC which consists of defective graphene acts as an electron delocalization amplifier from the CTP functional group that can work optimally when CTP is more attracted by the AC pores.

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