

ORIGINAL RESEARCH ARTICLE

Photocatalytic hydrogen production of Melon/Azodiphenylamine polymers

Jianhui Wang, Chengbo Fan, Yachao Zhai, Yuhao Tang, Haopeng Hou, Yaxin Zhu, Fengming Zhang*

College of Chemical and Environmental Engineering, Harbin University of Science and Technology, Harbin 150040, China. E-mail: zhangfm80@163.com

ABSTRACT

Hydrogen is one of the most attractive energy sources at present for its excellent properties, such as high energy density, clean and non-pollution energy. Photocatalytic hydrogen evolution is one of the ideal strategies to obtain hydrogen energy. This work aimed to improve the visible-light absorption ability of the structure similar to g-C₃N₄ by anchoring azo groups into the structure. By this, the photocatalytic hydrogen production rate of the resulting product was improved apparently. We use melamine as starting material to prepare Melon, which was further reacted with KOH, PCl₅ and 4,4-Diaminoazobenzene to get the target Melon/4,4-Diaminoazobenzene polymer. The condition influencing on the reaction was investigated, such as reaction temperature, the ratio of reactants and concentration of KOH solution. The structure of the as-synthesized polymer was determined IR, XRD, SEM, TGA and EIS. At the same time, its photocatalytic property was investigated.

Keywords: Hydrogen Evolution; Melon; Photocatalytic; g-C₃N₄

ARTICLE INFO

Received: 19 July 2021
Accepted: 12 September 2021
Available online: 16 September 2021

COPYRIGHT

Copyright © 2021 Jianhui Wang, *et al.*
EnPress Publisher LLC. This work is licensed
under the Creative Commons Attribution-
NonCommercial 4.0 International License
(CC BY-NC 4.0).
<https://creativecommons.org/licenses/by-nc/4.0/>

1. Introduction

Energy crisis and environmental pollution caused by the utilization of fossil energy are important problems in the process of China's economic and social development. The development and utilization of green, environmental friendly and renewable new energy is of far-reaching significance. Hydrogen has the advantages of high energy density, environmental friendliness and zero carbon emission. It is an ideal energy carrier. The calorific value of hydrogen combustion is three times that of gasoline, and its combustion product is only water^[1]. However, hydrogen production in industry is still dominated by coal gasification, heavy oil and natural gas, steam catalytic reforming and other processes. The production process involves a large number of fossil fuel consumption and greenhouse gas emissions. Although hydrogen production from electrolyzed water seems to avoid greenhouse gas emissions, its process consumes large amount of electric energy, has high cost, and will also cause environmental pollution when generating electric energy^[2]. If we can develop sustainable energy production and conversion technologies for hydrogen production in a green way and fundamentally solve the core scientific problems and technical bottlenecks of clean energy, it will play a positive role in promoting

the improvement of ecological environment. Photocatalytic hydrogen production is an effective way to obtain hydrogen in a green way. Solar energy is inexhaustible. Using solar energy to obtain hydrogen by photocatalytic decomposition of water is considered to be the most ideal way^[3].

The research on photocatalysts mainly focuses on heterogeneous semiconductor material systems, especially the traditional oxide such as TiO_2 ^[4-7] and CdS ^[8-10] with good photocatalytic performance and sulfide semiconductor photocatalysts^[11,12]. However, traditional semiconductor materials have a relatively single structure, lack appropriate proton activation sites and effective electron transfer paths. Thus, photo-generated electrons are easy to recombine with photo-generated holes, resulting in the loss of light quantum yield. In addition, most traditional semiconductors have a wide bandgap, only can be excited by ultraviolet light (about 4% of the solar spectrum), and the utilization rate of solar light is also low. In recent years, graphite phase carbon nitride (g- C_3N_4) as a pure organic polymer has the characteristics of high stability, low pollution, and non-metallic, and shows a good ability of visible light hydrolysis to produce hydrogen. However, the material has a narrow visible light adsorption range and low visible light utilization efficiency.

Given the above scientific problems, azo groups were constructed in similar g- C_3N_4 structures by step-by-step synthesis, which improved the visible light utilization efficiency of the materials, and its photocatalytic hydrogen production performance was significantly improved. In this paper, Melon was prepared from melamine, prepared into the salt mixing with KOH, chlorinated with PCl_5 , and finally reacted with azodiphenylamine to obtain Melon/azodiphenylamine polymer. The effects of temperature, KOH solution concentration and PCl_5 dosage on the preparation of polymer were studied, and the optimum experimental conditions were determined. The structure and morphology of the polymer were determined by characterization, and its photocatalytic properties were studied in detail.

2. Experiment

2.1 Reagents and instruments

Melamine (Sinopharm); phosphorus pentachloride (Shanghai Aladdin Biochemical Technology Co., Ltd.); 4-nitroaniline (Shanghai Aladdin Biochemical Technology Co., Ltd.); potassium peroxymonosulfonate (Shanghai Aladdin Biochemical Technology Co., Ltd.).

X-ray diffractometer (X' Pert PRO, panalytical analytical instruments, the Netherlands); muffle furnace (Tianjin City TAISITE Instrument Co. Ltd., SX-4-10); electric vacuum drying oven (Shanghai Experimental Instrument Factory Co., Ltd., ZK-82BB); infrared spectrometer (Perkin Elmer, Spectrum100); thermogravimetric analyzer (Perkin Elmer, STA6000); scanning electron microscope (FEI Sirion 200); photocatalytic activity evaluation system (CEAuLight, CEL-SPH2N).

2.2 Experimental methods

Firstly, 30 g of $\text{C}_3\text{H}_6\text{N}_6$ was calcined at 460 ~ 580 °C for 8 hours, and then cooled to room temperature to obtain Melon. After grinding, take 10 g of the product, add the powder into 200 mL, 2.5 M KOH solution, reflow the reaction for 4 hours, stand and cool the crystallization, filter under vacuum, and wash the crystallization repeatedly with absolute ethanol. The vacuum drying oven was set at 70 °C and dried for 8 hours to obtain the product potassium salt $\text{C}_6\text{N}_7(\text{OK})_3$. Mix 8 g of PCl_5 and 2.5 g of potassium salt powder and put them into the hydrothermal kettle. Put the hydrothermal kettle into the oven and raise the temperature to 220 °C. After solid-state reaction for 24 hours, take out the hydrothermal kettle and cool it to room temperature. The product is stirred in water at a temperature of <10 °C. The intermediate $\text{C}_6\text{N}_7\text{Cl}_3$ is obtained by suction filtration. Silica gel is added, dried and sealed, and then placed in the refrigerator for proper storage. The route is shown in **Figure 1**.

5 g of $\text{C}_6\text{H}_6\text{N}_2\text{O}$, 12.5 mL of sulfuric acid and 42.5 mL of water were mixed and stirred at 60–65 °C to prepare a solution. 20 g of $\text{H}_3\text{K}_5\text{O}_{18}\text{S}_4$ was slowly added within 1 h. The reaction continued under the conditions for 1 h. After vacuum filtration,

it was washed with distilled water repeatedly. The pH of the washing solution should reach neutral, and then dried at room temperature. Recrystallized with 80 mL glacial acetic acid and filtered to obtain a red needle like product. Add the product azodinitrobenzene and 40 g Na_2S into the solution prepared by 40 mL water and 120 mL ethanol, reflux the reaction for 30 min until precipitation is generated, cool and stand for 12 h. The filtered product was washed with water and allowed to stand at room temperature for 12 hours. Take 100 mL of ethanol to recrystallize the product and filter to obtain orange red crystalline azodiphenylamine. The product should be sealed and stored away from light. Finally, 2 g of $\text{C}_6\text{N}_7\text{Cl}_3$ was dissolved in 30 mL of toluene, 2.303 g of azodiphenylamine was added to it, wrapped with tin paper and stirred away from light for 24 h, reacted and refluxed at 125–135 °C for 2 h, filtered, washed with a mixture of toluene, acetone and water for many times, and dried naturally to obtain Melon/azodiphenylamine polymer (**Figure 2**). After grinding, the product was soaked in methanol to exchange solvent, and the final product was obtained after vacuum drying.

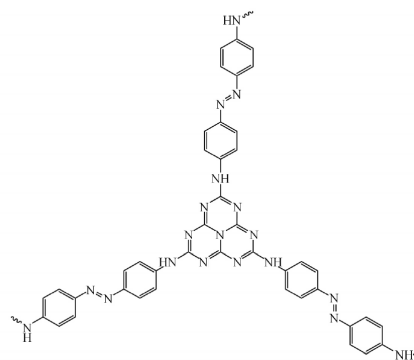


Figure 2. Schematic diagram of Melon/4,4-Diaminoazobenzene.

3. Results and discussion

3.1 Characterization analysis

The FTIR spectrum of the polymer is shown in **Figure 3**. It can be seen from **Figure 3** that $\text{C}_6\text{N}_7\text{Cl}_3$ reacts with azodiphenylamine to form a new substance. Through analysis, it can infer that the absorption peak at $3,500\text{ cm}^{-1}$ causes to the asymmetric stretching vibration of N–H of secondary amine. The absorption peak at $3,200\text{ cm}^{-1}$ is the asymmetric stretching vibration absorption peak of C–H on the benzene ring, and the four absorption peaks near $1,600\text{ cm}^{-1}$ and $1,500\text{ cm}^{-1}$ are caused by the skeleton vibration of the benzene ring, the stretching vibration of –N=N– bond and the stretching vibration of –C=N. The stretching vibration peak of –C–N appears at $1,300\text{ cm}^{-1}$, the bending vibration of –C–H produces absorption peaks at $1,250\text{ cm}^{-1}$, $1,150\text{ cm}^{-1}$ and $1,100\text{ cm}^{-1}$, and the absorption peak at 850 cm^{-1} proves to be para disubstitution. The sharp absorption peak can be seen from the XRD diffraction pattern (**Figure 3**). Therefore, it can infer that the product has

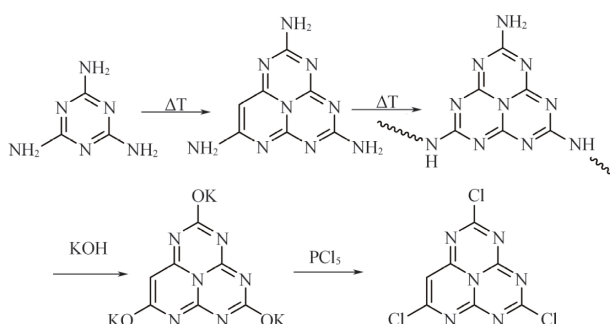


Figure 1. Synthetic method of $\text{C}_6\text{N}_7\text{Cl}_3$.

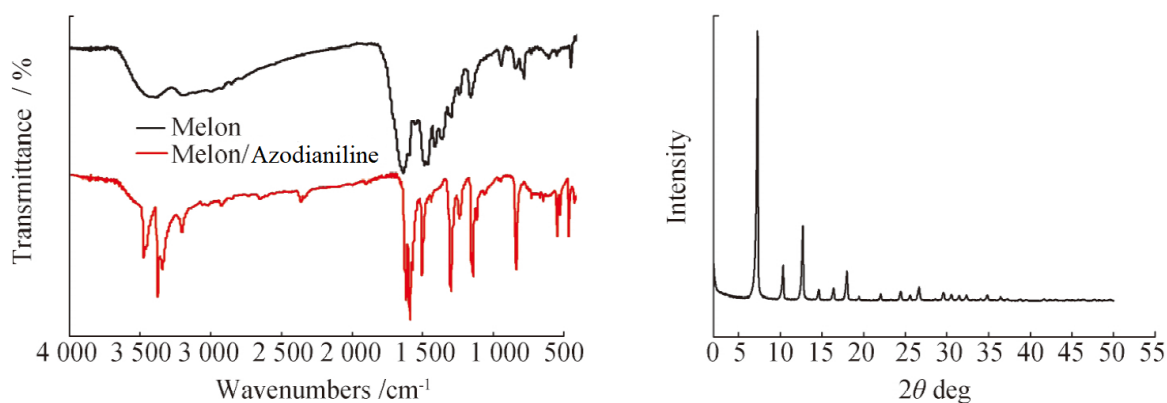


Figure 3. FTIR Spectra of Melon/4,4-Diaminoazobenzene and $\text{C}_6\text{N}_7\text{Cl}_3$, (left), XRD patterns of Melon/4,4-Diaminoazobenzene (right).

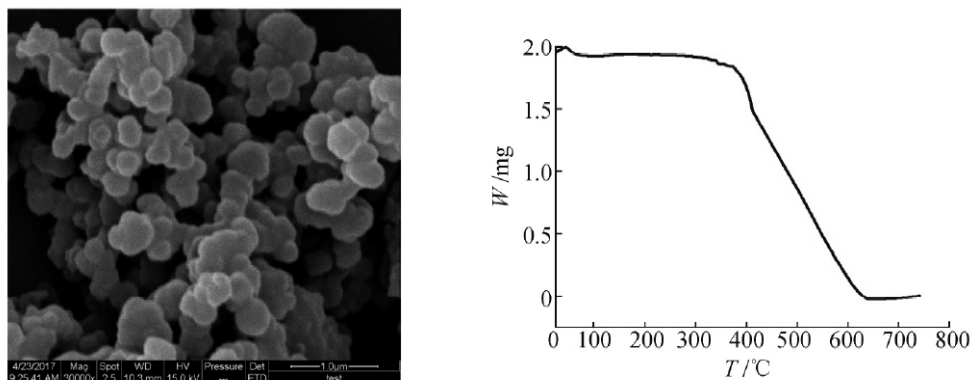


Figure 4. SEM images of Melon/4,4-Diaminoazobenzene with standard scale 1 μm (left) and TGA (right).

a good crystal structure and high crystallinity. High crystallinity can improve the catalytic activity of the catalyst. Therefore, it can be inferred theoretically that Melon/azodiphenylamine polymer has good photocatalytic activity.

To study the particle size and morphology of the polymer, it was analyzed by scanning electron microscope (SEM) (**Figure 4**). It shows from **Figure 4** that the appearance of the product presents a regular circular particle shape with a particle size of 0.2–0.4 μm . The particle size is relatively uniform. The particles are connected to form a loose and porous structure, and it has a large specific surface area, which is conducive to the photocatalytic reaction. At the same time, it carried out thermogravimetric (TGA) analysis to judge the thermal stability and thermal decomposition performance of the polymer (**Figure 4**). The thermogravimetric curve was divided into three sections. At the beginning of heating to about 50 $^{\circ}\text{C}$, the weight of the sample increases, which may be due to the adsorption of a small amount of gas. At 50–350 $^{\circ}\text{C}$, the adsorbed gas is resolved, the weight decreases and the sample has not been decomposed. When the temperature is more than 350 $^{\circ}\text{C}$, the sample begins to decompose. After heating to 400 $^{\circ}\text{C}$, the sample decomposes rapidly to complete. Therefore, Melon/azodiphenylamine polymer has good thermal stability at <350 $^{\circ}\text{C}$ and completely decomposes at >400 $^{\circ}\text{C}$.

3.2 Photocatalytic activity analysis

To study whether the polymer has good photocatalytic activity, the polymer was tested by EIS.

First, weigh 2 mg of Melon and Melon/azodiphenylamine respectively, put them into two ampoules, add 1 mL of absolute ethanol and 10 μL of tea phenol respectively, then ultrasound was performed for 30 min. Take two clean conductive glasses and use a pipette gun to take 200 μL Melon and 200 Melon/azodiphenylamine suspensions respectively and carefully drop onto the conductive glass, and the sample is successfully prepared after the solvent volatilizes. Using 0.5 M Na_2SO_4 solution as electrolyte, the test was carried out by three electrode system (reference electrode: saturated calomel electrode, auxiliary electrode: platinum electrode, working electrode: conductive glass attached to the sample). The EIS measurement results are shown in **Figure 5**. As can be seen from **Figure 5**, compared with Melon, Melon/azodiphenylamine has a smaller radius of curvature, which means that Melon/azodiphenylamine has less blocking effect on electron movement, which is conducive to electron migration. Therefore, it can be speculated that Melon/azodiphenylamine has better photocatalytic activity when exposed to light with the same energy.

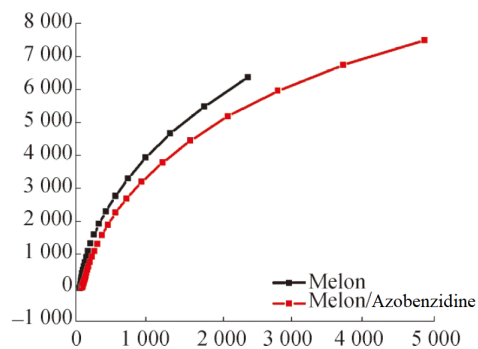


Figure 5. EIS graph of Melon and Melon/4,4-Diaminoazobenzene.

4. Photocatalytic hydrogen production performance test

In this paper, the photocatalytic hydrogen production properties of Melon and Melon/azodiphenylamine polymers were tested by CEL-SPH₂N photocatalytic activity evaluation system; in the test, xenon lamp is selected as the light source and triethanolamine as the sacrificial agent^[6], and the test is carried out by full spectrum irradiation.

Test the hydrogen production of Melon and Melon/azodiphenylamine polymers every 1 h^[7]. See **Figure 6** for the photocatalytic hydrogen production activity diagram of Melon and Melon/azodiphenyl-

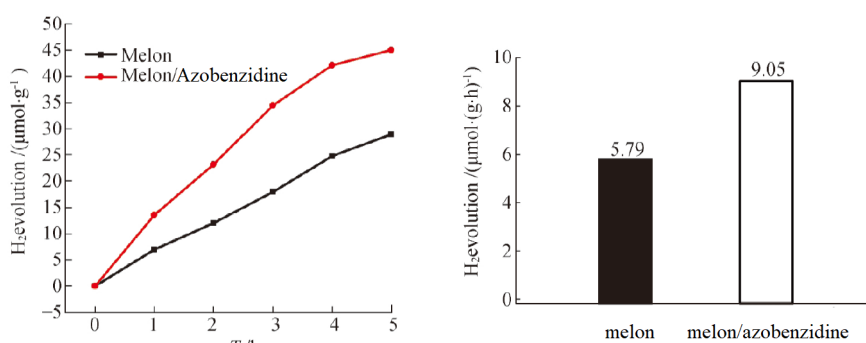


Figure 6. Photocatalytic activity diagram of hydrogen production (left) and Hydrogen production efficiency (right) of Melon and Melon/4,4-Diaminoazobenzene.

The comparison of hydrogen production efficiency between Melon/azodiphenylamine and Melon is shown in **Figure 6**. It can be seen from **Figure 6** that the hydrogen production efficiency of Melon/azodiphenylamine is 9.05 μmol/(g·h), which is 1.5 times that of Melon. Through the preliminary exploration of the photocatalytic hydrogen production performance of Melon/azodiphenylamine polymer and Melon, it is found that it has better photocatalytic hydrogen production performance than Melon.

5. Conclusion

In this paper, a Melon/azodiphenylamine polymer was synthesized. The polymer has the properties of 0.2–0.4 μm, uniform particle size, good crystal form and high crystallinity. The test data show that the polymer has good thermal stability and the blocking effect of electron movement is smaller than that of melon. The photocatalytic hydrogen production

amine. It can be seen from **Figure 6** that the hydrogen production of Melon/azodiphenylamine is higher than that of Melon. When illuminated for 5 h, the hydrogen production of melon is about 30 μmol/g, while the hydrogen production of Melon/azodiphenylamine is about 45 μmol/g, which is 1.5 times that of Melon. Compared with Melon, the photocatalytic hydrogen production activity of Melon/azodiphenylamine was significantly improved. However, the overall photocatalytic activity of Melon/azodiphenylamine was not as stable as Melon. Melon remained relatively stable at 0–5 h, while the activity of Melon/azodiphenylamine decreased significantly at 4–5 h.

performance of Melon/azodiphenylamine polymer was studied with triethanolamine as sacrificial agent. The results showed that the hydrogen production of Melon/azodiphenylamine polymer was 45 μmol/g, which is 1.5 times that of Melon. Improving the effect of polymer hydrogen production needs to be studied. This research work will provide new ideas for the development of new energy.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgements

Heilongjiang College Students' innovation and entrepreneurship training program (201710214039); the Youth Foundation of the National Natural Science Foundation of China (21501036).

References

1. Zhu Q, Xu Q. Liquid organic and inorganic chemical hydrides for high-capacity hydrogen storage. *Energy and Environmental Science* 2015; 8(2): 478–512.
2. Nasalevich MA, Becker R, Ramos-Fernandez EV, *et al.* Co@NH₂-MIL-125(Ti): Cobaloxime-derived metal-organic framework-based composite for light-driven H₂ production. *Energy and Environmental Science* 2015; 8: 364–375.
3. Toyao T, Saito M, Horiuchi Y, *et al.* Efficient hydrogen production and photocatalytic reduction of nitrobenzene over a visible-light-responsive metal-organic framework photocatalyst. *Catalysis Science & Technology* 2013; 3: 2092–2096.
4. Yin S, Han J, Zhou T, *et al.* Recent progress in g-C₃N₄ based low cost photocatalytic system: Activity enhancement and emerging applications. *Catalysis Science & Technology* 2015; 5(12): 5048–5061.
5. Sun Z, Kim JH, Zhao Y, *et al.* Rational design of 3D dendritic TiO₂ nanostructures with favorable architectures. *Journal of the American Chemical Society* 2011; 133(48): 19314–19317.
6. Wang G, Wang H, Li Y, *et al.* Hydrogen-treated TiO₂ nanowire arrays for photoelectrochemical water splitting. *Nano Letters* 2011; 11(7): 3026–3033.
7. Morgan DL, Liu HW, Frost RL, *et al.* Implications of precursor chemistry on the alkaline hydrothermal synthesis of titania/titanate nanostructures. *The Journal of Physical Chemistry C* 2010; 114(1): 101–110.
8. Fang Z, Liu Y, Shen J, *et al.* Epitaxial growth of CdS nanoparticle on Bi₂S₃ nanowire and photocatalytic application of the heterostructure. *The Journal of Physical Chemistry C* 2011; 115: 13968–13976.
9. Burch NC, Jasuja H, Walton KS. Water stability and adsorption in metal-organic frameworks. *Chemical Reviews* 2014; 114(20): 10575–10612.
10. Chen B, Xiang S, Qian G. Metal-organic frameworks with functional pores for recognition of small molecules. *Accounts of Chemical Research* 2010; 43: 1115–1124.
11. Hoang S, Guo S, Mullins CB. Coincorporation of N and Ta into TiO₂ nanowires for visible light driven photoelectrochemical water oxidation. *The Journal of Physical Chemistry C* 2012; 116(44): 23283–23290.
12. Li D, Soberanis F, Fu J, *et al.* Growth mechanism of highly branched titanium dioxide nanowires via oriented attachment. *Crystal Growth & Design* 2013; 13: 422–428.