Photo-thermo catalytic hydrogen production for solar full-spectrum storage with non-metal carbon nitride catalyst

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ABSTRACT

Photochemistry and thermochemistry are two ways to store solar energy into chemical energy directly. For photochemical process, the major challenge is that the catalyst cannot absorb the full spectrum of solar energy, and just the energy in short-wavelength spectrum can be stored while the energy in long-wavelength spectrum is wasted. Therefore, photochemistry has not yet been found widespread industrial adoption, in spite of decades of active research, because the relatively low solar photochemical efficiency. For thermochemical process, it often operates at relatively high temperature to achieve reasonable product yield, requiring high ratio concentrators and large mirror fields. To achieve higher solar-to-chemical efficiency on relatively mild condition, photo-thermo synergetic catalytic chemistry is proposed. In this work, we synthesized different kinds of non-metal carbon nitride catalyst for photo-thermo catalytic hydrogen production from water. The hydrogen generation rate is experimentally tested on photo catalytic condition, thermo catalytic condition and photo-thermo catalytic condition. Results show that the photo-thermo catalytic reaction rate is much bigger than the sum of the photo catalytic reaction rate and thermo catalytic reaction rate, which verifies the synergetic effect between the photo catalysis and thermo catalysis with non-metal catalyst. This work would inspire a pathway toward the chemical storage of solar fullspectrum energy.

Keywords: photo-thermo catalytic reaction; hydrogen production; solar full-spectrum storage; carbon nitride

NONMEN	CLATURE

PTC

Abbreviations

Photo-thermo catalysis

PCPhoto catalysisTCThermo catalysisSFSynergetic factorCNCarbon nitrideMMelamineAT3-amino 1, 2, 4-triazoleCCyanamide

1. INTRODUCTION

Solar energy is an ideal candidate to build an ecofriendly society because it is widespread and freely available. However, challenges associated with the intermittency of the solar flux lead to an increasing need for solar energy storage technologies. The idea of converting solar energy into chemical energy directly by photochemical process or thermochemical process has been considered to be a meaningful and attractive route.

Solar photochemical process is an old and fantastic idea. However, it has not been found widespread industrial adoption, in spite of decades of active research, because the relatively low solar photochemical efficiency outweighs the touted advantages of replacing heat with light [1]. A major problem for all photochemical process is that the absorptions of the catalysts cannot cover the full spectrum of solar energy. Just like the Shockley-Queisser limit setting on the silicon cell [2], the solar photochemical process exits a solar-tochemical efficiency limit since the long wavelength photons cannot be used.

On the other hand, most solar thermochemical reactions operate at relatively high temperature to achieve reasonable product yield, because of the large activation barrier associated with the rate-limiting step [3]. There are many negative side effects when running

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at high temperature. First, costly solar concentrators and mirror fields are required to concentrate more sunlight converted to thermal energy, because a significant input of heat is needed to run inherently exothermic chemical reactions. Second, the long-term stability of catalysts is compromised when the operating temperature is high. Third, the selectivity for the desired products decreases at higher operating temperature. Last but least, solar energy is converted to thermal energy firstly, then providing heat for chemical reactions. Two converting processes result in more irreversible loss.

To address these challenges, photo-thermo catalytic chemistry was proposed to achieve higher solarto-chemical efficiency in relatively mild conditions. The photo-thermo catalytic chemistry could be traced back to 1980s. The photo catalytic oxidation of isopropanol to propanone was studied using TiO₂ as catalyst at seven temperatures in the range of 277-313K, results showing that the reaction rate increased with the reaction temperature [4]. However, in the mainstream of photochemical researches, particular attention has been paid to the control of reaction temperature of photo catalytic process in order to minimize heating negative effect for a long time. In the recent years, thermal enhanced photochemical reactions and photons accelerated thermochemical reactions have been detected by researchers. For example, in the ethylene epoxidation, the reaction rate at 450 K and atmospheric pressure by photo-thermal catalytic process increases about fourfold compared to that of the individual thermal process. The rate enhancement in photothermo catalytic process was also detected in CO and NH3 oxidation, which means that photons could indeed help the oxidation reactions in thermochemical process [5]. In the experiment of benzene detoxification on TiO₂ and Pt/TiO₂ nanocomposite, the reaction rate by photo-thermo catalytic process at 240°C is greater than that by individual thermochemical process at 240°C or photochemical process at 40°C [6]. The synergetic effect between the photochemical process and thermochemical process is more obvious in the decontamination of gaseous styrene over LaMnO₃. The reaction rate by photo-thermo chemical process is 3.5 times the sum of the rate of photochemical process and the thermochemical process [7].

However, the researches related to the photothermo catalytic reactions are almost all based on the metal catalyst. In this work, the synergetic effect between the photochemistry and thermochemistry are verified over the non-metal catalyst for H_2 production.

2. EXPERIMENTAL

2.1 Materials and preparation

To verify the synergetic effect between the photo catalysis and thermo catalysis for hydrogen production with nonmetal catalyst carbon nitride, we synthesized three kinds of carbon nitride (CN) with different precursors, i.e., 3-amino 1, 2, 4-triazole (AT), melamine (M) and cyanamide (C). The synthesized catalysts are called AT-CN, M-CN, C-CN, respectively. The detailed procedures are shown as follows.

3.0 g precursor was mixed in 5 ml of deionized (DI) water and 0.5 mL HCl. The mixture kept stirring at 50°C until completely dissolved. Afterwards, 6 mL of 40 wt % of SiO₂ particles was added fast to the solution as a hard template. The obtained mixture was stirred at 80°C for several hours until water was evaporated. The composite of silica template and partially condensed precursor was transferred to a crucible and calcinated at a ramp of 10° C/min up to 500° C in N₂ atmosphere and maintained there at this temperature for another 4 h. 80 ml 4 M NH₄HF₂ solution was mixed with the resultant powder and the mixture was stirred for 36h at room temperature to dissolve the silica template. The obtained templatefree carbon nitride was centrifuged and washed with DI water and ethanol several times and dried at 75°C for 12h.

2.2 Structural Characterisation

The crystal structure of the prepared catalyst was characterized by X-ray diffraction (XRD). The wide-angle XRD was tested by a PAN-alytical X'Pert PRO diffractometer via Cu K α 1 radiation from 10° to 80° at a scan speed of 4° min⁻¹. Fourier Transform Infrared Spectroscopy (FT-IR) spectrum was characterized by a Nicolet 6700 spectrometer with a 4 cm⁻¹ resolution and 32 scans in the range of 4000-600 cm⁻¹. The ultravioletevisible (UV-vis) diffuse reflectance absorption spectra were tested on Agilent Cary 7000 Scan UV-vis spectrophotometer.

2.3 Photoeletrochemical test

The photoelectrochemical measurements was performed on a potentiostat (SP-300, BioLogic Science Instruments) in a standard three-electrode system. The catalyst based electrode was used as working electrode, which was prepared as follows. Catalyst (8 mg) was dispersed into 2 ml of the water isopropanol mixed solvent (4:1 v/v). Then 4ul nafion was added to the mixture. The mixture was sonicated for more than 30min until it formed a homogeneous suspension. The

prepared catalyst suspension was deposited uniformly onto Ti foil, which was dried to be used as working electrode. Pt-wire and Ag/AgCl (in saturated KCl) was used as counter electrode and reference electrode, respectively. The electrolyte was 100ml Na₂SO₃ aqueous solution (0.5 M). All potentials are converted into the NHE reference scale. The light source is 300 W Xenon arc lamp (LX300, Peccell Technologies, Inc.).

Photocurrent measurements were conducted at a constant potential of +1.0 V. Electrochemical impedance spectra (EIS) were carried out by applying 10 mV alternative signal over the frequency range from 1 Hz to100 kHz. The Mott-Schottky was measured at the potential range of -2V-0V in 0.5 M Na₂SO₄ aqueous solution at 1 kHz under dark conditions.

2.4 Hydrogen evolution

To verify the photo-thermo synergetic effect, we test the photo catalytic (PC) hydrogen production where the reaction is conducted in the light with the cycling water to cool the temperature of the reactant, the thermo catalytic (TC) hydrogen production in dark, and the photo-thermo catalytic (PTC) hydrogen production in light without cycling water. The light incident to the reactor, leading to the temperature of the reaction solution increasing. Then the photon energy and thermal energy are combined together to drive the reaction. In our experiment, the solution is heated up to $60^{\circ}C$ with the full light. If we use the recycling water to cool down the temperature, it is the normal photo catalytic reaction. As a comparable test, thermochemical reaction

is conducted in the dark at the same temperature of the photo-themo catalytic reaction.

The 300 W xenon arc lamp is adopted as the light source, which is installed about 30 cm from the liquid surface of the reactant solution. The reactant solution is prepared with 40 mg catalyst, 40 ml deionized water and 4 ml triethylamine. The inner diameter of the reactant container is 50 mm. Before reaction, the reactant solution is treated with Ar gas for 15 min and vacuumed for another 15 min. During the reaction, we analyze the producing gas every 30 min using a gas chromatograph equipped with a thermal conductivity detector. The N₂ gas is purged as carrying gas.

2.5 Evaluation parameter

Synergetic factor (SF) [8] is adopted to figure out the synergetic effect of photo catalysis and thermo catalysis intuitively. SF is calculated by the ratio of photo-thermo catalytic rate to the sum of photo catalytic rate and thermo catalytic rate. If SF > 1, there is synergetic effect between photo catalysis and thermo catalysis. Conversely, synergistic effect is not obvious.

3. RESULTS

3.1 *H*₂ *Production*

The hydrogen production rate on the photo catalytic condition, thermo catalytic condition and photo-thermo catalytic condition are presented in Fig. 1. It is clear that the photo-thermo catalytic hydrogen production is faster than both the single photo catalytic reaction and the single thermo catalytic reaction. The synergetic factor with all the catalyst is more than the 1, which means that

AT-CN PTC



Fig. 1 Comparison of hydrogen production rate among the photo-thermal catalysis, single photo catalysis and thermo catalysis.

the photo-thermo catalytic reaction rate is bigger than the sum of the single photo catalytic rate and single thermo catalytic rate. It indicates that the photo-thermo catalytic reaction is not simply the photo catalytic reaction adding to the thermo catalytic reaction or thermo catalytic reaction adding to thermo catalytic reaction, while there exits synergetic effect between the photo catalysis and thermo catalysis.

To study the effect of long-wavelength spectrum light, we test the hydrogen production with part of the spectrum. The hydrogen production with the light spectrum less than 500nm is slower than that with the full spectrum. The reason is that the photons used for photo catalytic reaction are less than those used with the full spectrum. The onset wavelength for the photo catalytic reaction is between 500 and 700nm. While, if the light with the spectrum is less than 700nm, the reaction rate is still smaller than that with the full spectrum. The number of the photons used for the photo catalytic reaction is the same with that used for the full spectrum. It can be indicated that the thermal energy generated by the long-wavelength spectrum of the light has a positive effect on the hydrogen production.



spectrum

3.2 Characterization of the catalyst

XRD were conducted to study the crystal structures of the prepared catalysts. It can be seen from Fig. 3 that the XRD peaks in this work are at 2 θ =13.2° and 27.5°, which could be indexed as the (002) and (100) planes of g-C₃N₄ (JCPDS 87-1526) [9]. The typical (002) peak around 27.5° indicates the graphite-like stacking of the conjugated aromatic units of CN with a distance of 0.324 nm, while the (100) peak reveals the in-plane structural packing motif of tris-triazine [10]. The two diffraction peaks agree with the bare g-CN.





The chemical structures of the catalysts was characterized by FT-IR spectra, which is shown in Fig. 4. The broad peak at the range of 2900-3500 cm⁻¹ indicates the stretching mode of N-H groups with vibration mode of an O-H attached to the aromatic ring, which is derived from the adsorbed water and uncondensed amine groups. The intense peaks appeared in the range of 1200-1700cm⁻¹, where the peaks at around 1238, 1314 and 1405 cm⁻¹ are attributed to the typical stretching vibration modes of the aromatic C-N while the peaks at around 1562 and 1603 cm⁻¹ are attributed to the stretching vibration of the aromatic C=N. The sharp peak at around 800 cm⁻¹ is assigned to the breathing vibration of triazine units, indicating that there existing triazine units in the local structure of the prepared catalysts.



3.3 Band structures

nerary

The UV-vis diffusion diffusion reflectance adsorption spectra is shown in Fig. 5. It seems that the absorption spectra of the AT-CN catalyst is wider than that of C-CN and M-CN. It is attributed to that the color of the AT-CN is a little bit deeper than C-CN and M-CN, contributing to the superior ability on absorbing visible light. The catalytic ability is complicated, and it is also related to the behaviors of photo carriers, charge diffusion pathway and active sites. Provide the second seco

Fig. 5 UV-vis diffusion diffusion reflectance adsorption spectra

4. CONCLUSION

In summary, we have studied the effect of the hydrogen production on the photo, thermal and photothermal reaction conditions over three kinds of carbon nitride catalysts. It was found that the hydrogen yield of the photo-thermal reaction is more than the sum of the related photo reaction and thermal reaction. The reaction rate under the full spectrum light is faster than that in the light spectrum without the long-wavelength spectrum. Results indicate that there exists synergetic effect between the photo catalysis and thermal catalysis, and the thermal energy generated by the longwavelength spectrum light can accelerate the photothermal reaction. This work would inspire a pathway toward the efficient hydrogen production with solar fullspectrum energy.

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