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FABRICATION OF HOLLOW 1D g-C_3N_4 PHOTOCATALYST FOR HYDROGEN PRODUCTION VIA WATER SPLITTING UNDER VISIBLE LIGHT IRRADIATION

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ABSTRACT

The simple and cost-effective method was adopted to prepare hollow 1D porous structure of g-C_3N_4 to generate hydrogen by photocatalysis. It plays a substantial role in efficient photocatalysis of water splitting. In general, the protonated melamine was calcined at high temperature to get 1D structure. It exhibits improvement in hydrogen evolution (2.54 mmol. $g^{-1}.h^{-1}$) in contrast to bulk g-C_3N_4 (0.10 mmol. $g^{-1}.h^{-1}$). Due to porous in nature, it has a high surface area (51.369 m^2g^{-1}) in contrast to bulk sample (7.73 m^2g^{-1}). Furthermore, 1D structure display low resistance against the charge transfer and have low recombination rate. These observations claiming that the hollow 1D porous structure play a crucial role to enhance photocatalytic activity.

Keywords: Photocatalyst, water splitting, hydrogen, visible light, renewable energy

NONMENCLATURE

Abbreviations	
XRD	X-Ray diffraction
FESEM	Field Emission Scanning Electron Microscopy
XPS	X-ray Photoelectron spectroscopy
FTIR	Fourier transform infrared
DRS	Diffuse reflectance spectra
EIS	Electrochemical Impedance Spectroscopy
PEC	Photoelectrochemical
Symbols	
λ	Wavelength

1. INTRODUCTION

The use of the primary energy resources caused serious concerns towards severe energy crisis worldwide [1]. The hydrogen production by photocatalyst has been extensively identified as an auspicious worthwhile technology with no hazardous carbon emissions which directly transform the renewable source like solar energy into hydrogen [2]. Previously, great progress has been made in developing many active photocatalyst but none of them was able to meet all the requirement for hydrogen production by solar energy efficiently. The important properties which make all the photocatalyst material inadequate to satisfy the industrial requirements are high visible-light quantum efficiency, low cost, efficient persistence. [3]. Consequently, there is an urgent need to improve the efficiency of already existing photocatalysts and find new photocatalyst having high quantum efficiency. Graphitic carbon nitride (g-C_3N_4) is considered as an innovative material and has attained comprehensive integrative consideration by virtue of its outstanding electronic, structural, and optical properties. It is a metal-free semiconductor photocatalyst operated by visible light for solar energy transformation and environmental pollution reduction. [4]. However, some key factors like high charge recombination, low surface area, and limited active sites effect the efficiency of the g-C_3N_4 semiconductor [5]. Many studies have been reported so far to bypass these restraints and improve the photocatalytic performance of g-C_3N_4 including doping, exfoliation of 2D nanosheets, addition of a heteroatom, morphological tuning, heterojunction, defects engineering and surface plasmonic resonance effect [5]. In the last few years, one dimensional (1D) structures attracts great attention of the researchers due to its large surface area, high length to diameter ratio that can reduce the charge diffusion length, enhance the light harvesting and also exploits the usage of incident photons due to multiple reflections. It includes nanorods, nanowires, and nanotubes having exceptional properties. For example, the nanomaterials with a tubular structure can transfer the charge carriers along the 1D path and provide a high

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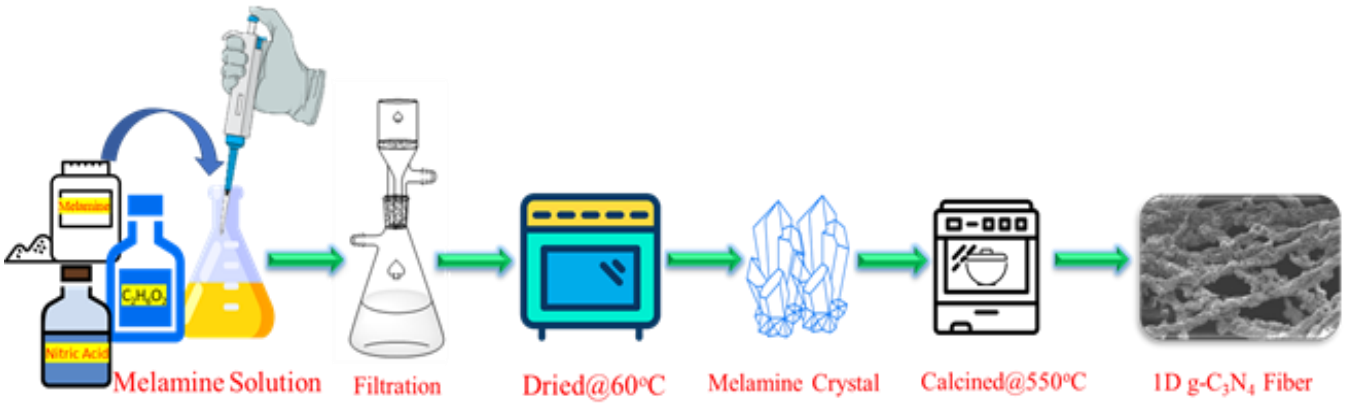

Fig 1 Schematic illustration of synthesis method of Hollow 1D g-C_3N4

surface area for photocatalytic reaction. Hence, the modification of g-C_3N_4 with 1D structure can be helpful for future hydrogen generation. Here in this study, we develop a 1D hollow structure of g-C_3N_4 by simple template free method that have increased the surface area, optical properties, reduce the recombination rate and enhance the hydrogen production about 24.9 times than the bulk g-C_3N_4. Briefly this study focusses on the structural tuning of the g-C_3N_4 photocatalyst to improve its photocatalytic performance under solar light irradiation.

1.1 Material and methods

Firstly, 2g melamine was added in 30ml ethylene glycol and stirred in an oil bath at 80°C to completely dissolved. After that 50ml of 0.2M HNO_3 was added slowly during stirring at room temperature. The white thick solution was washed with DI water and ethanol several times and dried it at 60°C for 12h. The dried powder was calcined in air atmosphere at 550°C for 2h with a ramp rate of 12°Cmin^{-1} and named it 1D g-C_3N_4. The bulk g-C_3N_4 sample was also prepared for comparison by heating melamine at 550°C for 2h with a heating rate of 12°Cmin$^{-1.}$

1.2 Characterization

XRD pattern were examined by X'pert MPD Pro (PANanalytical Co), using Cu Kα radiation (40 kV, 40 mA). FESEM) images were taken by JEOL JSM 6700F instrument. The surface area was obtained by Nitrogen adsorption-desorption isotherms method using ASAP 2020 instrument. UV-vis DRS is done by PE lamba 950 spectrometer operating between 850 and 240nm wavelengths. $BaSO_4$ was used as reflectance sample. The XPS data was obtained using Thermo Fisher ESCALAB Xi+ (USA) instrument (Al (mono) X-ray source), while the binding energy were calibrated using C 1s = 284.7eV. The FTIR data were recorded by using TENSOR II infrared spectrometer (Bruker) and KBr as reference.

1.3 Photoelectrochemical measurement

The electrochemical measurements were conducted on an electrochemical workstation. The EIS was noted under AC amplitude of 5mV and the frequency range from 0.1Hz to 1000Hz. The transient photocurrent was measured using 0.5V bias voltage under light illumination of 300W Xe lamp (λ>420nm).

1.4 Photocatalytic Hydrogen Production

The hydrogen production test was done under visible light. 0.025g of photocatalyst was dispersed in 50ml solution of water and TEOA (10%vol) with 2%wt Pt. The air was removed by providing nitrogen gas for 10 min. The amount of H_2 was measured by gas chromatography (Agilent Technologies: 6890 N) with TCD equipped with a 5Å molecular sieve using N_2 as the carrier gas. The

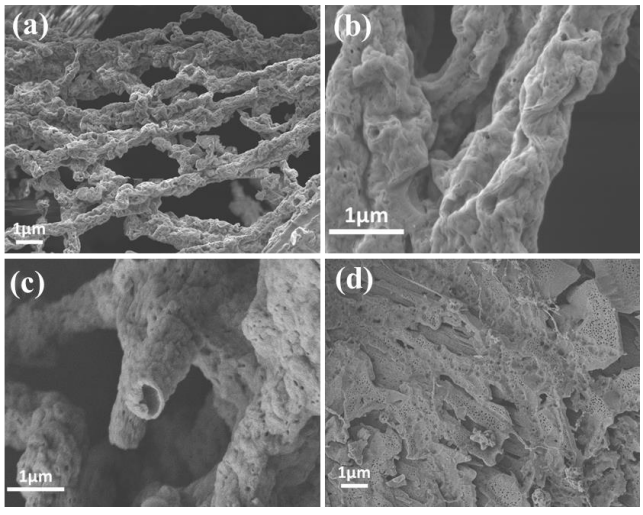

Fig 2 SEM (a-c) 1D g-C_3N_4, (d) Bulk g-C_3N_4

reaction system is bubbled with N_2 30 minutes before every cycle during lifetime evaluation test.

1.5 Results and Discussion

The schematic illustration of the synthesis method was shown in fig 1. The FESEM images (fig 2) shows the textural structure of the prepared samples. Fig 2a, b displays the 1D porous structure of g-C_3N_4. Fig 2c depicts that the fiber was hollow, and several pores present on the surface that is mainly due to the massive oxidative gas emissions during calcination process. Fig 2d shows the structure of bulk g-C_3N_4 that consist of many nanosheets.

The phase and structural characteristics were measured by XRD as shown in fig 3a. Both the samples display two peaks at about 27° (200) plane that is due to the interlayer stacking of aromatic segments and other is at 13° (100) plane relates to the interplanar structural packing of tri-s-triazine units.

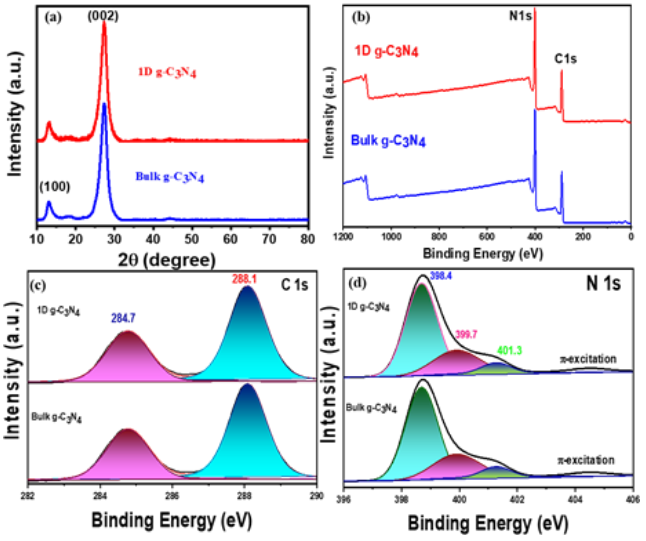

Fig 3 (a) XRD (b) XPS Survey, (c,d) HR XPS

The chemical state and composition of the samples is investigated by XPS. Fig 3b shows the survey spectrum of both the samples that indicate the presence of C and N which is well matched with the XRD results. The high resolution XPS data C1s and N1s (Fig 3c, d) indicates that there is no obvious energy shift, suggesting that both the samples have same chemical states. FTIR spectroscopy was carried out to examine the chemical structure of the prepared samples as shown in fig 4. Both the samples have similar spectra and all the absorption band is indicating the presence of g-C_3N_4. The peak at 808 cm^{-1} represents the s-triazine unit while the peaks at band range of 1233-1639 cm^{-1} is attributed for the stretching vibration band of C-N heterocycle [7]. The broad peak at 3169 cm^{-1} indicating about the stretching vibrational and deformation modes of N-H [8].

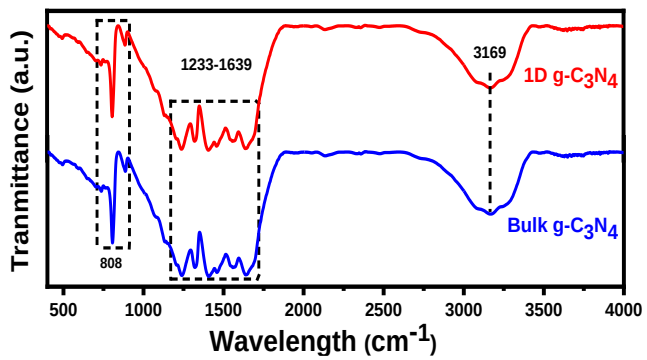

Fig 4 FTIR Spectra of sample 1D g-C_3N_4 and Bulk g-C_3N_4

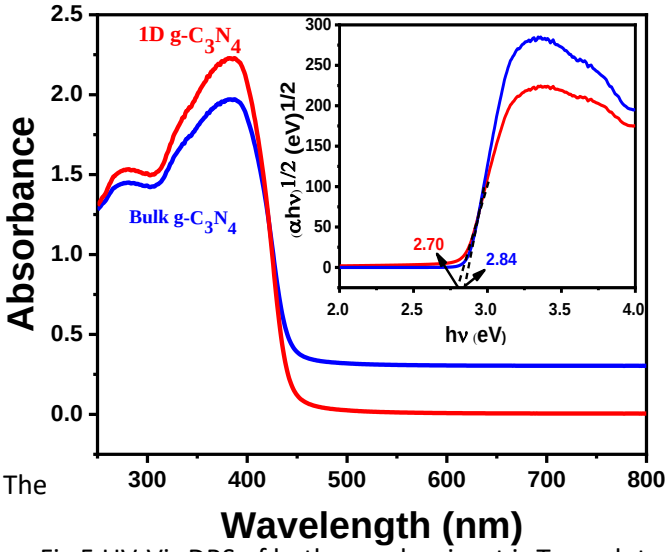

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Fig 5 UV-Vis DRS of both samples, inset is Tauc plot

UV-Vis DRS were used to study the optical properties of the samples. Fig 5 indicates that both the samples absorb light in the visible region but 1D-g-C_3N_4 sample shows a high absorption intensity than bulk g-C_3N_4 due to its 1D structure which may causes multiple reflection and scattering. The bandgap energy was found by Tauc's plot (inset of fig 5) that depicts 1D-g-C_3N_4 has band gap of 2.70eV while bulk g-C_3N_4 shows 2.84eV. These finding suggested that the treated melamine at different solvent could not only change the structure but also effect the optical properties. The specific surface area was measured by nitrogen adsorption desorption isotherms as shown in fig 6. The curve of both the samples indicates the type IV isotherms and type H3 hysteresis loop. The 1D porous sample shows a very high surface area about 51.369 m^2g^{-1} while bulk sample have only 7.781 m^2g^{-1}.The inset of fig 6 shows the pore volume

and pore radius of 1D g-C_3N_4 (0.314 cm^3 and 6.4nm) and bulk g-C_3N_4 (0.093 cm^3 and 6.7nm) respectively.

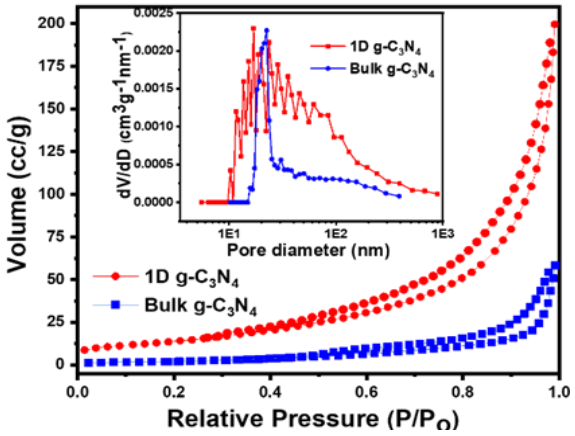

Fig 6 Nitrogen adsorption-desorption of both samples, inset is BJH pore size distribution

EIS was studied to find the charge separation and transfer in the prepared samples. The Nyquist plot (fig 7a) shows that 1D g-C_3N_4 sample curve have smallest diameter, so it has a lower resistance against the transfer of electron. Fig 6b shows that 1D g-C_3N_4 sample have the highest transient photocurrent density than bulk g-C_3N_4 which exhibits fast movement of electrons. The results of PEC measurements suggested that 1D structure of g-C_3N_4 reduces the recombination rate and help to increase the photocatalytic activity.

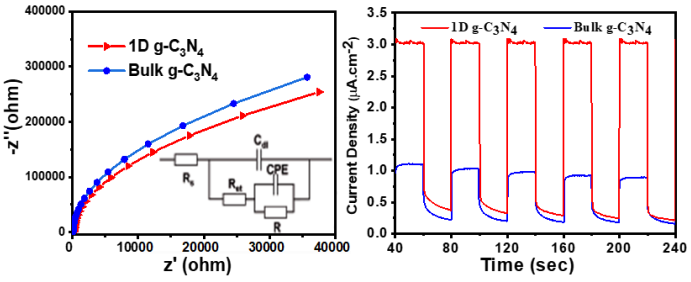

Fig 7 PEC measurement Test (a) EIS curve, inset is the equivalent circuit (b) Transient Photocurrent

The Hydrogen evolution by water splitting under visible light irradiation of both the samples is shown in fig 8a. It can be clearly seen 1D g-C_3N_4 sample delivered highest hydrogen production which is about 2.54 mmol. $g^{-1}.h^{-1}$ in comparison to bulk g-C_3N_4 0.10 mmol. $g^{-1}.h^{-1}$. It is important for the photocatalyst practical application to sustain its stability for a long time. Fig 8b demonstrated that 1D g-C_3N_4 sample exhibit workable photocatalytic performance after five cycles without any loss in the hydrogen generation rate.

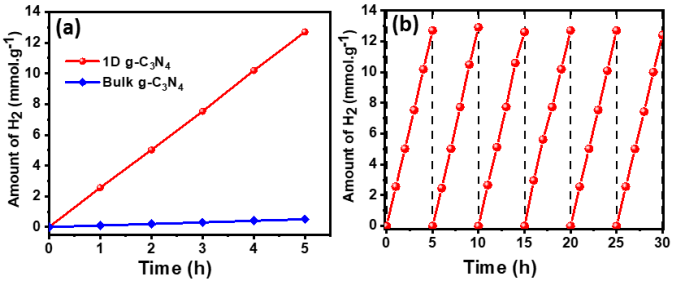

Fig 8 (a) Hydrogen Evolution of both samples (b) Cyclic Test of H_2 Evolution for 1D g-C_3N_4

1.6 Conclusions

In summary, we have successfully fabricated a hollow 1D structure of g-C_3N_4 that have evolved good amount of hydrogen by water splitting under visible light. The high photocatalytic performance of 1D sample is primarily due to the high surface area, large pore volume and fast charge transfer of electrons. In future, we can use this structure to study further modification techniques for the sake of improving photocatalytic activity.

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