New insight of the photocatalytic behaviors of graphitic carbon nitrides for hydrogen evolution and their associations with grain size, porosity, and photophysical properties

Junghoon Oh[a], Jang Mee Lee[b], Youngjun Yoo[c], Jeongho Kim[c], Seong-Ju Hwang[b], Sungjin Park[a],*

[a] Department of Chemistry and Chemical Engineering, WCSL (World Class Smart Lab) Green Energy Battery Lab., Inha University, 100 Inha-ro, Nam-gu, Incheon, 22212, Republic of Korea
[b] Department of Chemistry and Nanoscience, College of Natural Sciences, Ewha Womans University, Seoul, 03760, Republic of Korea
[c] Department of Chemistry and Chemical Engineering, Inha University, 100 Inha-ro, Nam-gu, Incheon, 22212, Republic of Korea

ARTICLE INFO

ABSTRACT

The development of efficient catalysts for hydrogen evolution reaction (HER) presents a huge technical challenge. Graphitic carbon nitride (g-C_3N_4) is a promising metal-free, low cost, environment-friendly photocatalyst for HER that is driven by visible light. In this work, the authors provide new insight into the photocatalytic natures of g-C_3N_4 materials and their dependences on grain size, porosity, chemical structure, and photophysical properties. Three different precursors (urea, melamine, and dicyandiamide) and two gas atmospheres (air or N_2) are used to produce various g-C_3N_4 materials. The use of urea and air leads to the formation of small grain C_3N_4 networks and porous structures with large surface areas. HER catalytic activity is promoted by large surface areas and the presence of terminal amine groups, and generation of small-sized Pt nanoparticle co-catalysts with narrow size distribution on the surface of g-C_3N_4. For samples with similar surface areas, band gaps and lifetimes of photogenerated charge carriers critically determine photocatalytic activities. By examining combinations of the above-mentioned factors, urea driven g-C_3N_4 produced in a N_2 atmosphere is found to exhibit the best photocatalytic activity (up to 130 μmol h^{-1} g^{-1}).

1. Introduction

Hydrogen evolution reaction (HER) is essential for water-splitting in various renewable and environment-friendly energy storage systems and requires efficient catalysts to overcome the activation energy required [1–5]. Reports on the electrochemical photolysis of water using TiO_2 particles led to the developments of various semiconducting materials [1], such as, MoS_2 [6–9], $MoSe_2$ [10], WS_2 [11,12], and $CoSe_2$ [13] and carbon-based nanomaterial [13–16] hybrids of these with excellent HER photocatalytic performances. Specifically, visible light-active photocatalysts can be energetically favorable because visible light constitutes ~40% of solar photons [17,18]. However, the development of metal-free, low-cost, environment-friendly catalysts remains a considerable challenge.

Carbon nitride (C_3N_4)-based materials have generated research interest as possible efficient and metal-free photocatalysts for HER [3,4,19–22]. Graphitic C_3N_4 (g-C_3N_4), which is composed of triazine or tri-s-triazine building units, is the most stable type of C_3N_4-based materials. They have been often reported to have excellent performances when used as photocatalysts [3,4,19–22], bioimaging probes [23,24], and optical sensors [25] due to a band gap of ~2.7 eV, which is suitable for use with visible light, numerous nitrogen sites, and their porous structures. Wang et al. demonstrated a possible application of g-C_3N_4 as a metal-free photocatalyst for HER based on experimental and theoretical investigations [20]. In this previous study, g-C_3N_4 was produced by thermal condensation of a cyanamide precursor and showed good catalytic activity for HER under visible light. Subsequently, tuning of the band gap by doping with heteroatoms [26,27] and increasing surface areas using template-assisted processes indicated the potential use of g-C_3N_4 based materials as efficient catalysts [28,29].

Recently, the control of porosity and morphology of g-C_3N_4 without the use of templates has attracted attention as a means of making materials in a cost-effective, predictable way. It has been shown that adjustments of temperature and/or time of polycondensation can be used to control structural and catalytic properties. While polymeric C_3N_4 is typically produced at 550 °C, Lau et al.

reported that heat treatment of melamine at 450 °C for long time can afford melem oligomer containing increased active sites, and the materials produced showed enhanced HER photocatalytic performances [4]. Kang et al. found that sequential thermal treatment of dicyandiamide at 500 °C and 620 °C produced amorphous C_3N_4, which has a wider absorption range for visible light [22]. Furthermore, post-heat treatment (at 580 °C) of g-C_3N_4 powder produced by the thermal treatment of dicyandiamide at 510 °C, broke hydrogen bonds between C_3N_4 domains in the g-C_3N_4 network, and resulted in the production of porous g-C_3N_4 materials containing more active sites and significantly greater photocatalytic activity [3]. In addition, several workers have reported the use of urea as precursor leads to the production of porous C_3N_4 materials with excellent catalytic performances [30–34].

However, the dependencies of the morphological and structural characteristics of C_3N_4-based materials on synthetic approaches (precursor type, temperature, time, and the gaseous environment) preclude detailed understanding of their photocatalytic natures. In the present study, we produced and characterized a series of g-C_3N_4 materials from various precursors in different gaseous environments to explore dependences of the photocatalytic natures of g-C_3N_4 materials on grain size, porosity, chemical structure, optical and photophysical properties, and size distribution of Pt nanoparticles as co-catalysts.

2. Experimental

2.1. Preparation of graphitic carbon nitrides (g-C_3N_4s) in air (CN-A)

Urea (99%), dicyandiamide (99%), and melamine (99%) powders were purchased from Sigma-Aldrich. Each precursor (2, 10, and 10 g for urea, dicyandiamide, and melamine, respectively) was loaded into an alumina crucible, which was then placed in the center of a quartz tube. The tube was heated to temperatures near the boiling point of each precursor (150, 350, and 250 °C for urea, melamine, and dicyandiamide, respectively) at a rate of 3 °C/min and then held at these temperatures for 1 h under an air flow in a muffle furnace. The temperature was then elevated to 550 °C at 3 °C/min and held for 2 h (air flow was maintained). The prepared g-C_3N_4s were denoted as U-CN-A, M-CN-A, and D-CN-A (where U, M, and D represent urea, melamine, and dicyandiamide, respectively, and A represents air). The quartz tube was then cooled to room temperature, to afford pale yellow powders (72 mg for U-CN-A, 1.3 g for M-CN-A, and 3.2 g for D-CN-A).

2.2. Preparation of graphitic carbon nitrides in N_2 (CN-N)

All processes were the same as described above except that N_2 (99.9%) was used instead of air. Before starting experiments, the quartz tube containing precursors was vacuum degassed and filled with N_2. Final g-C_3N_4 products were obtained as pale yellow powders (92 mg for U-CN-N, 3.7 g for M-CN-N, and 5.3 g for D-CN-N, N represents N_2). The g-C_3N_4s obtained were used without further purification.

2.3. The photocatalytic activities of the materials produced

Photocatalytic activities were investigated in a top-irradiated vessel connected to a gas circulation system. As synthesized g-C_3N_4 powder (100 mg) containing 3 wt% of Pt co-catalyst was suspended in 100 ml of an aqueous solution containing 10 vol% triethanolamine as a sacrificial agent. The mixture was then irradiated using a 300 W Xe lamp (Newport Stratford Inc.) fitted with an optical cut-off filter ($\lambda > 420$ nm). Amounts of H_2 evolved were determined with gas chromatography (Shimadzu GC-2014).

2.4. Band position calculation

Band positions of g-C_3N_4s were determined using CV curves obtained using a potentiostat IVIUMSTAT (Ivium Technologies, USA) and a conventional three-electrode cell. A Pt mesh and Ag/AgCl electrode (+0.198 V vs NHE) were used as a counter and reference electrodes, respectively, and 0.5 M Na_2SO_4 was used as electrolyte. The working electrodes were prepared by doctor blading a material with the help of Nafion binder on a FTO substrate.

2.5. Characterization

X-Ray photoelectron spectroscopy (XPS) was performed using an angle-resolved X-ray photoelectron MXR1 Gun spectrometer operated at 400 μm and 15 kV (Theta probe, Thermo Fisher Scientific, UK); the analysis was performed with sample attached by copper tape and binding energies were determined versus the N 1s peak at 398.8 eV. Peak fitting was conducted using a mixed Gaussian-Lorentz product function after subtraction of a linear background from the spectra. Full width half maximum (FWHM) parameter with 1.35 eV was used to adjust peak fitting.

Elemental analysis was conducted using a FLASH EA1112 instrument (Thermo Electron, Italy) for C, N, H, and a Vario Micro Cube (Elementar Analysensyteme GmbH, Germany) for oxygen. X-ray diffraction (XRD) patterns were obtained using a DMAX-2500 unit (Rigaku, Tokyo, Japan). Photoluminescence (PL) spectra were obtained using a spectrograph ($f = 0.5$ m, Spectrograph 500i, Acton Research Co., USA) equipped with an intensified CCD (PI-MAX3, Princeton Instruments, IRY1024, USA) and He-Cd 325 nm laser. Fourier-transform infrared (FT-IR) spectra of samples in KBr pellets were obtained using 64 scans of an FT-IR vacuum spectrometer (VERTEX 80 V, Bruker, Germany). Nitrogen adsorption–desorption measurements were carried in a Micromeritics ASAP 2010 device at 77.3 K. The surface area and pore diameter were obtained using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. Transmission electron microscopy (TEM) images, selected area electron diffraction (SAED), and energy-dispersive X-ray spectroscopy (EDS) were obtained using a JEOL JEM2100F instrument (JEOL Co. Ltd., Japan) at 200 kV equipped with an EDAX analyzer (INCA X-stream Oxford Instruments, UK). Samples for TEM analysis were prepared by drying a droplet of a mixture including g-C_3N_4 powder in water on a carbon-coated copper grid (LC300-Cu, Electron Microscopy Sciences). Scanning electron microscopy (SEM) images of Pt-coated samples were obtained using a high resolution field emission scanning electron microscope (SU 8010, Hitachi, Tokyo) at an accelerating voltage of 15 kV. Thermogravimetric analysis (TGA) measurements (SDT Q600, TA Instruments) were performed at a heating rate of 5 °C/min from 30 to 800 °C in a N_2 environment. UV–vis diffuse reflection spectra were obtained using a UV-2600 (Shimadzu, Japan) equipped with an ISR-2600 Plus integrating sphere attachment. Time-resolved photoluminescence (TR-PL) was measured using a time-correlated single photon counting spectrometer (FluoTime 200, PicoQuant) at room temperature. All samples prepared with pellet type were excited using 100 ps laser pulses of 390 nm center wavelength and emission was performed at 500 nm. The nominal temporal resolution of TR-PL measurements was ∼190 ps.

3. Results and discussion

In this work, we prepared six g-C_3N_4 samples by solid-state high-temperature polycondensation using three common monomers (melamine, dicyandiamide, and urea) in two gas environments (air or N_2). We first measured the HER photocatalytic performances of all g-C_3N_4 materials under visible light.