RAPID COMMUNICATION

Thermal vapor condensation of uniform graphitic carbon nitride films with remarkable photocurrent density for photoelectrochemical applications

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Abstract
Graphitic carbon nitride (g-CN) is a promising material for photoelectrochemical (PEC) H₂ generation due to its appropriate band gap, low cost and nontoxicity. However, current techniques, including drop casting and spin coating, fail to deposit uniform g-CN films on solid substrates. In this work, we report on a thermal vapor condensation method of depositing uniform g-CN films on various substrates using melamine as a single precursor. Surface morphology and film thickness of the g-CN film can be effectively tuned by changing the substrate and precursor mass, respectively. The g-CN film shows photocurrent density as high as 0.12 mA cm⁻², the highest to date for g-CN based photoanode, at the bias of 1.35 V versus reversible hydrogen electrode (RHE) with Na₂S as the sacrificial reagent. The improved photoresponse of the g-CN film results from intimate contact between the film and the substrate, enhanced light absorption, decreased charge transport and charge transfer resistance with the increase of the process temperature. The success enables the g-CN films being effectively applied in multiple electronic and photoelectronic devices.

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Introduction

Photoelectrochemical (PEC) water splitting for H₂ production by semiconductors has received a great deal of attention, since using H₂ can ease the pressure of the energy crisis and alleviate the increasing environmental problems associated with this [1]. Ideally, photoelectrode materials should have strong absorption of visible light, efficient charge separation and transport properties, and suitable redox and oxidation potentials for water splitting [2]. However, most semiconductors cannot meet all these criteria at the same time. TiO₂ is the most investigated photoanode material because of its superior stability and appropriate conduction and valence band positions [3,4]. Nevertheless, TiO₂ can only absorb light in the UV region due to its wide band gap (3.0 and 3.2 eV for rutile and anatase phases, respectively). Therefore, doping [5], combining with narrow band gap semiconductors [6,7], and dyes are needed to enhance the photoresponse of TiO₂.

Recently, graphitic carbon nitride (g-CN) has been considered as a good photocatalyst for solar fuel conversion and pollutant degradation due to its moderate band gap of 2.7 eV, good chemical stability under light irradiation, low cost, and nontoxity [9]. Considerable work has been done to optimize its production have been hindered by the significant challenge of deposition of uniform g-CN films on solid substrates. To date, synthesis of g-CN has mainly been achieved by thermal condensation of different precursors (such as melamine [17], thiourea, [11] and cyanamide [8]) and always the g-CN powders were obtained. The “films” derived from depositing the g-CN powders on substrates through spin-coating [18] or drop-casting [19] have poor photoresponse (only several μA/cm²) due to the weak adhesion force between g-CN and the substrate. Shalom and coworkers have developed a method which involves placing the substrate below the precursor to deposit the g-CN nanostructures on it [20-23]. Liu and coworkers developed a strategy combining nanoconfined chemical vapor deposition and microcontact printing to deposit patterned g-CN films on substrates. They introduced the precursor into the anodic aluminum oxide (AAO) template and placed the template between two pieces of FTO glass [24]. Nevertheless, improvement in the uniformity of these films is needed for more reliable functionality.

Very recently, we developed a thermal vapor condensation (TVC) method, which can be used for deposition of large area uniform g-CN films [25]. Herein, we report successful synthesis of uniform g-CN films on different substrates including FTO glass, ITO glass, silica and glass by TVC. The PEC properties of the g-CN films and the influence factors including process temperature, mass precursor and sacrificial reagent are systematically investigated. Due to the intimate contact between the g-CN film and the substrate, low charge transport and transfer resistance, the photocurrent density is up to 0.12 mA cm⁻² at the bias of 1.35 V (versus RHE) with Na₂S as the sacrificial reagent. To the best of our knowledge, this is the best performance for g-CN film based photoanode, indicating the great potential of g-CN films as photoanode materials for PEC water splitting.

Experimental details

All the chemicals in this work were purchased from Acros without additional statement. In a typical synthesis, 50 g of melamine was put into a ceramic crucible (200 mL). Before the experiment, the crucible was well polished using an abrasive sheet. A piece of FTO glass of 10 cm, 10 cm and 0.32 cm, respectively, in length, width, and height, was uniformly covered on the top of the ceramic crucible. Then they were placed in a muffle furnace (carbolite) and maintained at 500 °C, 550 °C, and 600 °C for 3 h in air with heating and cooling rates of 3 °C/min. To facilitate the description, the g-CN films processed under 500 °C, 550 °C, and 600 °C are referred to in the rest of this paper as g-CN500, g-CN550, and g-CN600, respectively. ITO glass, silica and glass were also used as substrates. Dicyandiamide, thiourea and urea were further attempted as precursors for deposition of the g-CN film.

Drop casting and spin coating were also used to fabricate the g-CN film. g-CN powder fabricated at 600 °C was milled for 20 min by mortar. Then 0.2 g of the fine powder was dispersed in 30 mL of ethanol. Then it was ultrasonically treated for 10 min and following kept static for another 10 min. For drop casting, 10 droplets of the dispersion liquid were dropwise added on the surface of FTO glass. And then it was placed in the oven at 80 °C for 20 min. The same process was repeated for five times. For spin coating, the spin rate was 900 rpm and the process was repeated for 10 times. Then the FTO glasses were placed in oven at 80 °C for 20 min.

Surface morphologies of the g-CN films on FTO glass were measured on a Quanta F400 85-field emission scanning electron microscope (FE-SEM). X-ray diffraction (XRD) patterns were recorded using a Philips powder diffractometer (Cu Kα, λ = 1.5406 Å). Surface and three-dimensional morphologies of the g-CN films on ITO, silica and glass and the thickness of the g-CN films was measured by an Atomic Force Microscope (AFM) (VEECO Multimode V) with nanoscope V controller. X-ray photoelectron spectroscopy (XPS) was performed on the XPS (PHI Model 5802) with Al Kα radiation and the peaks were calibrated by C1s at 284.6 eV. Fourier Transform Infrared (FTIR) spectra were measured using the FTIR Spectrometer (Perkin-Elmer Spectrum 100). The UV-vis absorption spectra of the g-CN films were recorded by the UV-vis spectrophotometer (Varian 50 Conc).

The PEC properties of the g-CN films were measured in a commercialized PEC cell. The g-CN films were cut to small pieces and the edges of the films were sealed by epoxy resin before measurement. The photoresponses of the films were recorded on a three-electrode electrochemical workstation (CHI 760E), in which the g-CN film, Pt sheet, and Ag/AgCl electrode (filled with saturated KCl at 20 °C, 4.6 M) were used as the working, counter, and reference electrodes, respectively. The potentials versus Ag/AgCl were converted to those versus RHE according to the Nernst equation (E_RHE = E_Ag/AgCl + 0.059pH + 0.197). Unless stated otherwise, the electrolyte used in the experiment contained 0.1 M Na₂SO₄ (alpha), 0.1 M Na₂SO₃ (alpha) and 0.01 M Na₂S (pH = 11.6). The electrolyte was purged with N₂ for 0.5 h before measurement. The electrochemical impedance spectra (EIS) were recorded in the dark and under light at 0.5 V in the frequency region of 0.1–10⁵ Hz with AC voltage of 10 mV. A Xe lamp (NewBet) with AM 1.5 filter (100 mW/cm²) was used as the light source. To measure the incident photon conversion...