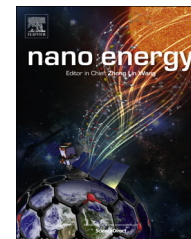


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RAPID COMMUNICATION

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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1 Introduction

3 Photoelectrochemical (PEC) water splitting for H₂ production
4 by semiconductors has received a great deal of attention,
5 since using H₂ can ease the pressure of the energy crisis and
6 alleviate the increasing environmental problems associated
7 with this [1]. Ideally, photoelectrode materials should have
8 strong absorption of visible light, efficient charge separation
9 and transport properties, and suitable redox and oxidation
10 potentials for water splitting [2]. However, most semicon-
11 ductors cannot meet all these criteria at the same time. TiO₂
12 is the most investigated photoanode material because of its
13 superior stability and appropriate conduction and valence
14 band positions [3,4]. Nevertheless, TiO₂ can only absorb light
15 in the UV region due to its wide band gap (3.0 and 3.2 eV for
16 rutile and anatase phases, respectively). Therefore, doping
17 [5], combining with narrow band gap semiconductors [6,7],
18 and dyes are needed to enhance the photoresponse of TiO₂
19 nanostructures in the visible range [8].

20 Recently, graphitic carbon nitride (g-CN) has been consid-
21 ered as a good photocatalyst for solar fuel conversion and
22 pollutant degradation due to its moderate band gap of 2.7 eV,
23 good chemical stability under light irradiation, low cost, and
24 nontoxicity [9]. Considerable work has been done to optimize its
25 catalytic performance, such as doping [10,11], forming het-
26 erojunctions with different semiconductors [12,13], decorat-
27 ing with metal nanoparticles [14] and copolymerization
28 [15,16]. Unfortunately, applications of g-CN in PEC fuel
29 production have been hindered by the significant challenge
30 of deposition of uniform g-CN films on solid substrates. To
31 date, synthesis of g-CN has mainly been achieved by thermal
32 condensation of different precursors (such as melamine [17],
33 thiourea, [11] and cyanamide [8]) and always the g-CN
34 powders were obtained. The “films” derived from depositing
35 the g-CN powders on substrates through spin-coating [18] or
36 drop-casting [19] have poor photoresponse (only several μA/
37 cm²) due to the weak adhesion force between g-CN and the
38 substrate. Shalom and coworkers have developed a method
39 which involves placing the substrate below the precursor to
40 deposit the g-CN nanostructures on it [20-23]. Liu and co-
41 workers developed a strategy combining nanoconfined chemi-
42 cal vapor deposition and microcontact printing to deposit
43 patterned g-CN films on substrates. They introduced the
44 precursor into the anodic aluminum oxide (AAO) template
45 and placed the template between two pieces of FTO glass
46 [24]. Nevertheless, improvement in the uniformity of these
47 films is needed for more reliable functionality.

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

2 Experimental details

62 All the chemicals in this work were purchased from Acros
63 without additional statement. In a typical synthesis, 50 g of
64 melamine was put into a ceramic crucible (200 mL). Before the
65 experiment, the crucible was well polished using an abrasive
66 sheet. A piece of FTO glass of 10 cm, 10 cm and 0.32 cm,
67 respectively, in length, width, and height, was uniformly
68 covered on the top of the ceramic crucible. Then they were
69 placed in a muffle furnace (carbolite) and maintained at 500 °C,
70 550 °C, and 600 °C for 3 h in air with heating and cooling rates
71 of 3 °C/min. To facilitate the description, the g-CN films
72 processed under 500 °C, 550 °C, and 600 °C are referred to in
73 the rest of this paper as g-CN500, g-CN550, and g-CN600,
74 respectively. ITO glass, silica and glass were also used as
75 substrates. Dicyandiamide, thiourea and urea were further
76 attempted as precursors for deposition of the g-CN film.

77 Drop casting and spin coating were also used to fabricate
78 the g-CN film. g-CN powder fabricated at 600 °C was milled
79 for 20 min by mortar. Then 0.2 g of the fine powder was
80 dispersed in 30 mL of ethanol. Then it was ultrasonically
81 treated for 10 min and following kept static for another
82 10 min. For drop casting, 10 droplets of the dispersion liquid
83 were dropwise added on the surface of FTO glass. And then it
84 was placed in the oven at 80 °C for 20 min. The same process
85 was repeated for five times. For spin coating, the spin rate
86 was 900 rpm and the process was repeated for 10 times. Then
87 the FTO glasses were placed in oven at 80 °C for 20 min.

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

103 The PEC properties of the g-CN films were measured in a
104 commercialized PEC cell. The g-CN films were cut to small
105 pieces and the edges of the films were sealed by epoxy resin
106 before measurement. The photoresponses of the films were
107 recorded on a three-electrode electrochemical workstation
108 (CHI 760E), in which the g-CN film, Pt sheet, and Ag/AgCl
109 electrode (filled with saturated KCl at 20 °C, 4.6 M) were used
110 as the working, counter, and reference electrodes, respectively.
111 The potentials versus Ag/AgCl were converted to those versus
112 RHE according to the Nernst equation ($E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + 0.197$). Unless stated otherwise, the electrolyte used in the
113 experiment contained 0.1 M Na₂SO₄ (alfa), 0.1 M Na₂SO₃ (alfa)
114 and 0.01 M Na₂S (pH=11.6). The electrolyte was purged with N₂
115 for 0.5 h before measurement. The electrochemical impedance
116 spectra (EIS) were recorded in the dark and under light at 0.5 V
117 in the frequency region of 0.1-10⁵ Hz with AC voltage of 10 mV.
118 A Xe lamp (NewBet) with AM 1.5 filter (100 mW/cm²) was used
119 as the light source. To measure the incident photon conversion
120
121
122
123

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