Full Length Article

Manipulation structure of carbon nitride via trace level iron with improved interfacial redox activity and charge separation for synthetic enhancing photocatalytic hydrogen evolution

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A B S T R A C T

Manipulation structure of graphitic carbon nitride (GCN) to tune its photophysical and interfacial redox activity is one of fundamental issues for understanding and improving its photocatalytic hydrogen evolution (PHE) activity. In this work, we report our recent progress on manipulating structure of GCN via an easy and effective approach. Trace level iron is found to have increased atomic concentration and tuned bond state of carbon in structure manipulated GCN (M-GCN) along with porosity of it, which exhibits higher interfacial redox and photophysical activity than GCN. The improved interfacial redox and photophysical activities of M-GCN are found to have synthetic enhanced consumption of photo-generated electrons and holes during photocatalysis process and reduction of their recombination, which results in promotion of its PHE activity. PHE rate for M-GCN is found to be $2286\,\mu\mathrm{mol}^{-1}\,\mathrm{g}^{-1}\,\mathrm{h}^{-1}$, which is 2.82 time of GCN.

1. Introduction

After persistent involvement in decades, works on improving photocatalytic activity of semiconductor materials have achieved great progress [1,2]. The broad prospects of artificial photosynthesis such as splitting water to generate hydrogen as clean energy carrier [3,4] has boosted explosive increase of novel nanostructure semiconductor materials with photocatalytic hydrogen evolution (PHE) activity [5–7]. By tuning photophysical characters of these semiconductor materials, their PHE activity was largely improved [8–10]. Within all reported photocatalysts, metal free semiconductor graphitic carbon nitride (GCN) has been intensively studied for its environmental compatibility and visible light PHE activity [11,12]. However, poor PHE activity of it has been major obstacle on its way to practical applications. Thus, understanding the relationship between its structure and PHE activity would be of fundamental importance for further developing GCN based highly active PHE photocatalysts [13–15].

PHE reaction involves photophysical and interfacial redox process [16]. In previous works, research focusing on photophysical process of GCN has proved that pristine GCN strongly localizes photo-generated

electrons in its basal plane, which resulted in hardness of photo-generated electrons accessing surface active sites to produce molecular hydrogen [17]. To overcome this obstacle, large amount of work focusing on engineering band structure of GCN via constructing type II [18–20], Z-scheme [21] heterojunctions with other semiconductor materials to improve charge separation and reduce recombination of them or enhance light absorption via surface plasmonic resonance through depositing noble metal [22,23] have been reported. In compared with abundant experiment and theoretical researches on photophysical characters of GCN, the important role of interfacial redox process on its PHE activity has been noticed very recently. Platinum (Pt) [24], Ni_2P [25], NiS [26] and CoP [27] based co-catalysts, which are highly effective on boosting PHE activity of GCN, have been studied. It was found that improved reduction activity of electrons or oxidation activity of holes on these co-catalysts of GCN composites plays crucial role on increasing PHE activity. Moreover, our recent research have shown that compositing Co/N doped carbon nanotubes with GCN can enhance both electron and hole reaction kinetics for improving PHE activity of GCN [28]. Besides, sacrificial electron donors [29] and electrolytes that facilitate hole reaction kinetics [30] were also
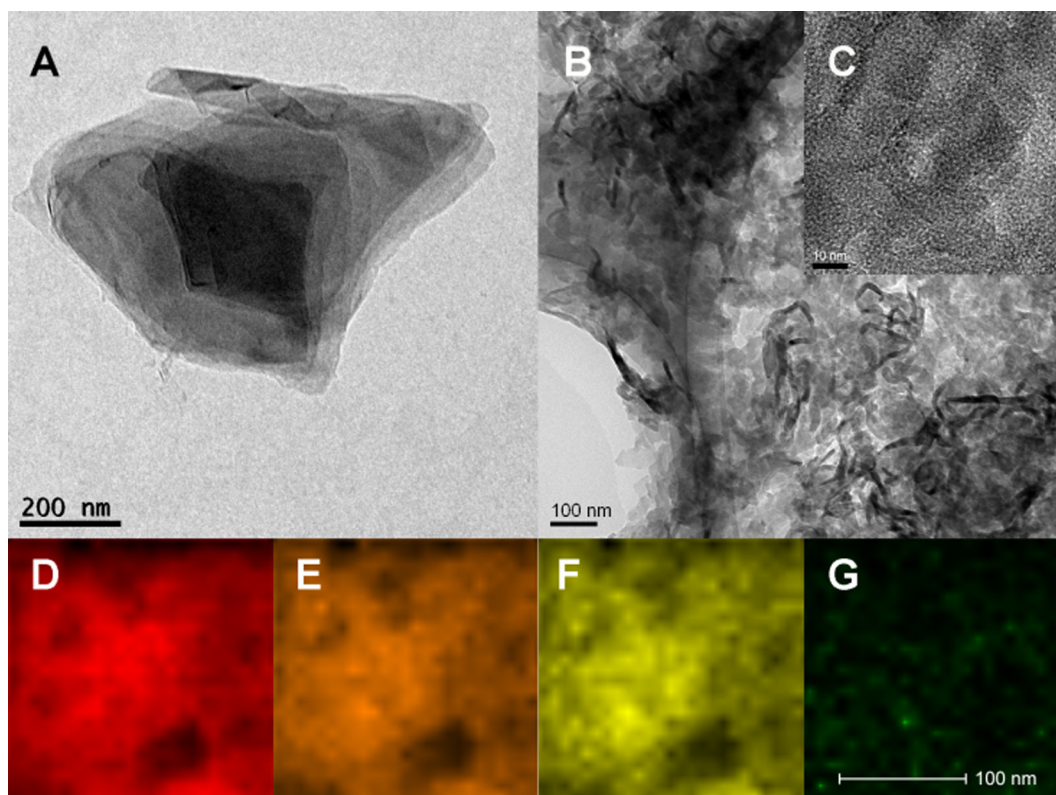
Fig. 1. TEM image of (A) GCN and (B) M-GCN, inset (C) is enlarged HR-TEM image of M-GCN, scale bar 10 nm, Elemental mappings for (D) Carbon, (E) Nitrogen, (F) Oxygen and (G) Fe in M-GCN, scale bar 100 nm.

found to be important on effective improving PHE activity of GCN based catalysts. All these recent involvements in GCN based catalysts have provided more comprehensive and profound understanding of its PHE process [31,32].

It worth to be noticed that if intrinsic catalytic activity of GCN has not been fully explored, enhanced PHE of it via adjusting PHE environment or introducing co-catalysts would be limited. To boost PHE of GCN, manipulating structure of GCN would be of great interest and can provide fundamental insight of its structure-activity relationship. Manipulating structure of GCN via non-metal dopants [33] such as doping sulphur [34], phosphorus [35,36], carbon [37,38] or alkali metal [39] and transitional metal [40] doping along with surface activation of GCN [41,42] have recently been intensively studied. Some research works has shown that not only band structure but also interfacial redox activity of GCN has been changed [34,35,41], which is important for improving PHE activity of GCN. Our recent research has directly point out that GCN with increased basal plane defects that facilitate hole oxidation kinetics can promote its PHE activity [43].

Inspired by recent progress of GCN based photocatalysts, we proposed an easy and effective approach to manipulate structure of GCN. Structure manipulated GCN (M-GCN) synthesized by introducing Fe during pyrolysis process of urea have shown obviously increased atomic concentration of carbon and distorted structure of M-GCN. Photophysical and photo-electrochemical analysis have shown synthetic role of charge separation and interface redox activity of M-GCN on enhancing its PHE activity. As separation of photo-generated electrons/holes within M-GCN and consumption of them on interface of GCN were improved, effectively enhanced PHE activity under visible light irradiation was achieved.

2. Experimental

2.1. Materials

Urea and all other reagents for synthesis and analysis were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of photocatalysts

The preparation process of photocatalysts and Pt deposition has been described in our previous works [28]. In brief, GCN was prepared by pyrolysis of 10 g urea at 550 °C for 3 h with temperature increase rate of 10 °C min^{-1}. The preparation of M-GCN is followed same thermal treatment program while 1 mg FeCl$_3$·6H$_2$O was added into 10 g urea. The obtained M-GCN (or GCN) was washed by deionized water and dried. Then 100 mg of dried M-GCN (or GCN) was dispersed in 100 mL deionized water followed by adding 0.3 mL H$_2$PtCl$_6$·6H$_2$O (10 mg mL^{-1}) and 2 mL acetic acid (1 mol L^{-1}) and N$_2$ bubbled for 1 h to remove oxygen followed by 300 W Xe lamp irradiated the dispersion for three hours, The resulting 3 wt% Pt-M-GCN (or Pt-GCN) was obtained by washing by ethanol and deionized water and drying at 60 °C overnight.

2.3. Characterization and measurement

TEM (Tecnai G2 F20S-TWIN at 200 kV), XRD (Bruker AXS D8-Focus), XPS (X'Pert-Pro MPD using Cu Kα (λ = 1.5406 A), ICP-MS (PerkinElmer Elan DRC-e), FT-IR (Thermo Scientific Nicolet iS50) and element analysis (Elementar Analysensysteme GmbH vario EL cube) were used to characterize structure and composition of catalysts. UV–Vis DRS (Hitachi UV-3600) and PL (FLS920, excitation wavelength of 325 nm) were used to characterize photophysical characters of catalysts.