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Ultrathin graphitic C_3N_4 nanofibers: Hydrolysis-driven top-down rapid synthesis and application as a novel fluorosensor for rapid, sensitive, and selective detection of Fe^{3+}

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ABSTRACT

Ultrathin graphitic C_3N_4 (g-C_3N_4) nanofibers about 5–10 nm in diameters have been rapidly prepared via alkali-catalyzed hydrolysis of bulk g-C_3N_4 in concentrated alkaline aqueous solution. The morphologies of the g-C_3N_4 nanostructures can be facilely controlled by varying reaction time, and a scissoring mechanism is proposed to explain the formation process involved. The g-C_3N_4 nanofibers can serve as a novel fluorosensor for rapid Fe^{3+} detection with high sensitivity and selectivity.

1. Introduction

As the most stable allotrope of carbon nitride, graphitic C_3N_4 (g-C_3N_4) polymer possesses a stacked 2D structure with excellent chemical and thermal stability under ambient conditions [1,2]. g-C_3N_4 is green, sustainable, and can be facilely synthesized in large scale with low cost by polycondensation of various carbon and nitrogen-containing organic precursors [3–5]. In recent years, g-C_3N_4 has been widely used in photocatalysis and photovoltaics [6–12], bioimaging [13], sensing [14–20], and electrocatalytic oxygen reduction [21–24], etc.

Materials at nanoscale level may exhibit a range of unusual properties when compared with their bulk counterparts [25]. Recent researches have also shown that nanostructured g-C_3N_4 exhibits superior properties to bulk g-C_3N_4 (b-g-C_3N_4). For example, although b-g-C_3N_4 possesses high photoluminenscence intensity, its low photoresponsivity and macroscopic size prevents its application in bioimaging. Such limitation can be overcome by using g-C_3N_4 nanosheets [14]. Yang et al. have shown that g-C_3N_4 nanosheets not only provide abundant reactive sites for hydrogen evolution, but increase transport of charges and reduce the ecombination probability of photoexcited charge carriers, owing to their large aspect ratios and high surface area [26].

Till now, ultrasonication-assisted liquid exfoliation [10,13,16–18,26] and thermal oxidation etching [9] of b-g-C_3N_4 have been developed recently for top-down fabrication of g-C_3N_4 nanosheets. The former method, however, suffers from the requirement of long period of reaction time. The latter method suffers from the use of high reaction temperature and extremely low yield. Cui et al. have developed a solvothermal approach toward g-C_3N_4 nanobelts about 50–60 nm in width by polymerizing cyanuric chloride and melamine in subcritical acetonitrile solvent [27]. This method is still pretty time-consuming and the used cyanuric chloride and acetonitrile precursors are toxic [28]. Thus, developing a toxicity-free approach for rapid synthesis of nanostructured g-C_3N_4 is highly desirable but challenging.

The employ g-C_3N_4 as sensors for heavy metal ions detection has caused increased attention largely due to its fluorescent property. Recently, several groups have demonstrated the use of different g-C_3N_4 nanostructures for fluorescent metal ions sensing [14–16]. Iron is the most abundant essential transition metal ion in the human body and acts an important role in many biochemical processes [29–31]. It is used by many proteins for oxygen transport, electron transport, and catalyzing oxido-reductase

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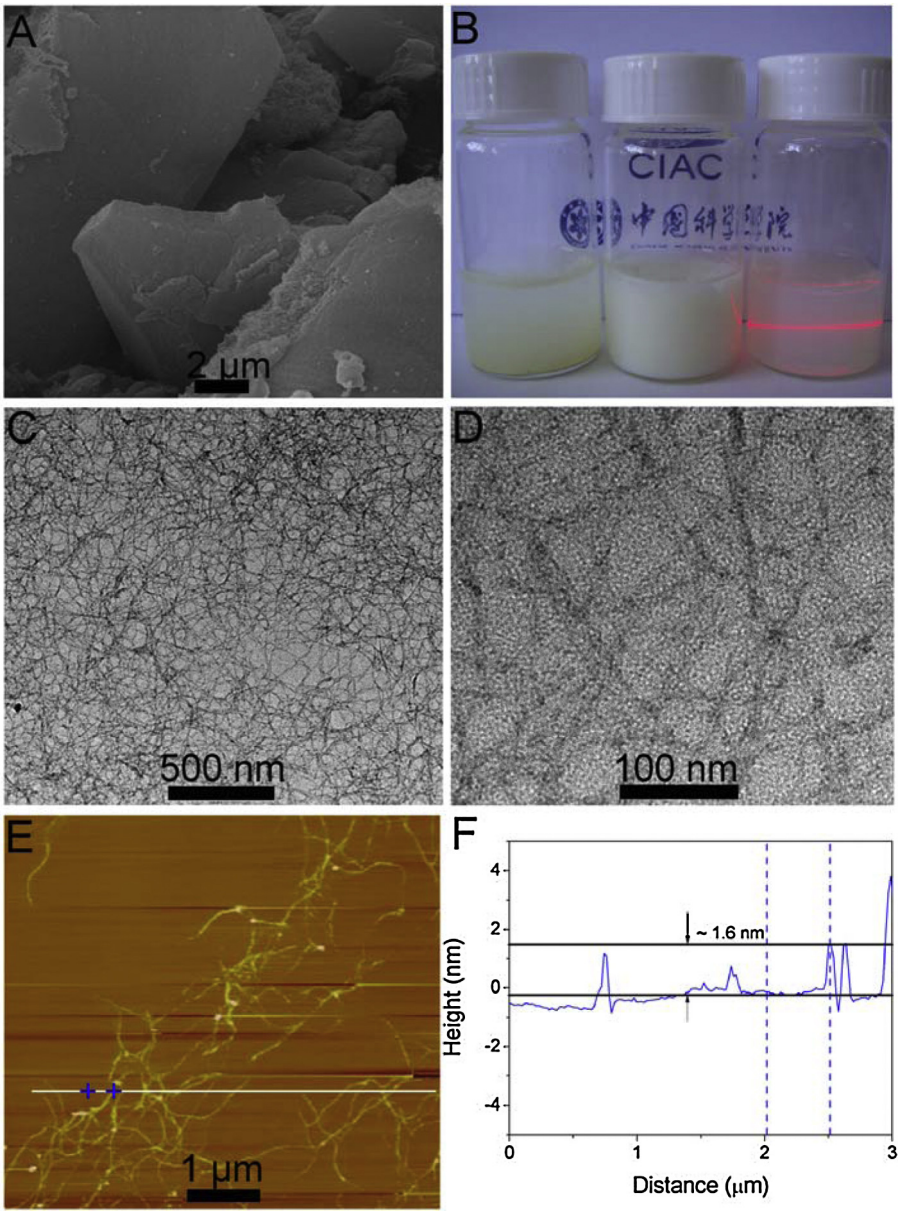

Fig. 1. (A) Typical SEM image of the b-g-C_3N_4. (B) Optical photographs of b-g-C_3N_4 dispersion in 8 M NaOH aqueous solution before (left) and after (middle) 2-h hydrolysis. Tyndall effect exhibited by g-C_3N_4 nanofibers dispersion passed through with red laser light (right). (C) Low and (D) high magnification TEM images of the g-C_3N_4 nanofibers. (E) AFM image of g-C_3N_4 nanofibers and (F) the corresponding section analysis of several random nanofibers. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

reaction [32]. A iron deficiency results in fatigue, poor work performance, and decreased immunity, but excess amounts of iron in a living cell is connected with serious diseases, including Alzheimer's, Huntington's and Parkinson's disease [33,34]. Thus, quantitative determination of Fe^{3+} is of great significance. So far, several methods have been developed for Fe^{3+} detection, including atomic absorption spectrometry, voltammetry, colorimetry and fluoremetry, etc. [35–41]. In this work, for the first time, we demonstrate a hydrolysis-driven top-down synthesis of ultrathin g-C_3N_4 nanofibers about 5–10 nm in diameters via alkali-catalyzed hydrolysis of b-g-C_3N_4. The nanofiber formation is rapid and completed in 2 h at 80 °C in concentrated alkaline aqueous solution. The morphologies of the g-C_3N_4 nanostructures can be facilely controlled by varying reaction time, and the formation mechanism involved is proposed. We further show the application of such g-C_3N_4 nanofibers as a novel fluorosensor for rapid, sensitive, and selective detection of Fe^{3+}.

2. Experimental

2.1. Reagents and materials

KOH, NaOH, $NaNO_3$, KNO_3, $Ca(NO_3)_2$, $Co(NO_3)_2$, $Cu(NO_3)_2$, $FeCl_2$, $Al(NO_3)_3$, $BaCl_2$, $Fe(NO_3)_3$, $Hg(NO_3)_2$, $Mn(NO_3)_2$, $Ni(NO_3)_2$, $Pb(NO_3)_2$, and $Zn(NO_3)_2$ were purchased from Beijing Chemical Corp. Melamine, Tris and HCl were purchased from Aladdin Ltd. (Shanghai, China). All chemicals were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

2.2. Preparation of ultrathin g-C_3N_4 nanofibers

Bulk g-C_3N_4 (b-g-C_3N_4) was first prepared by direct pyrolysis of melamine in the semiclosed system. In a typical synthesis, 10 g of melamine was placed in an alumina crucible with a cover and then