

## Short Communication

## Preparation and characterization of poly-hydrogen cyanide nanofibers with high visible light photocatalytic activity

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## ABSTRACT

Poly-hydrogen cyanide (PHC) nanofibers were prepared by directly heating the formamide (HCONH<sub>2</sub>) in a stainless-steel autoclave at 200 °C. The composition and structure of the products were characterized by X-ray diffraction, transmission electron microscopy, UV–vis diffuse reflectance spectrum, thermogravimetric analysis, Fourier transform IR, Raman and X-ray photoelectron spectroscopy. The results showed that the as-prepared nanofibers are graphite-like structure C/N ratio of 1.23. The as-prepared nanofibers exhibited higher photocatalytic activities by degradation of methyl orange (MO) than N-TiO<sub>2</sub> under visible light irradiation.

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## 1. Introduction

Since the theoretical predictions of Liu and Cohen, carbon nitride is of current interest due to its unique properties, including low density, extreme hardness, wear resistance, chemical inertness, biocompatibility and special optical and electrical properties [1,2]. Especially, polymeric graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) has been actively studied as a novel metal-free photocatalyst for photocatalytic energy conversion. This material has become the focus of considerable research activities [3–5]. As a photocatalyst, it also exhibits activity for the photodegradation of organic pollutants in solution [6] or in air [7] under visible light irradiation. Since the g-C<sub>3</sub>N<sub>4</sub> photocatalyst possesses high thermal and chemical stability, it is a valuable and useful material for applications.

Many experimental studies have attempted to produce dense crystalline C<sub>x</sub>N<sub>y</sub> phases, by using various techniques, including high-pressure and high-temperature (HP-HT) synthesis [8–10], chemical vapor deposition etc. [11,12]. Most researchers have prepared this versatile inorganic polymer from carbon and nitrogen containing compounds like cyanamide, dicyandiamide, urea and melamine etc. [13–15]. However, the photocatalytic efficiency of bare g-C<sub>3</sub>N<sub>4</sub> is still limited due to the high recombination rate of photo-generated electron–hole pairs. So many researchers have modified g-C<sub>3</sub>N<sub>4</sub> by nonmetal doping [16,17], noble metal deposition [18,19] and preparation of nanoporous g-C<sub>3</sub>N<sub>4</sub> [20,21]. To our best knowledge, no work has been focused on its morphological control and photocatalytic properties.

Here, we report the synthesis of the poly-hydrogen cyanide nanofibers (PHC-NFs) by directly heating the formamide in a stainless-steel autoclave and exploration of their photocatalytic activities. The PHC-NFs show excellent activity in photodegradation of MO under visible light irradiation.

## 2. Experimental section

In a typical synthesis, 60 ml of formamide was poured into a 100 ml stainless-steel autoclave. The autoclave was maintained at 200 °C for 48 h, and then air cooled to room temperature. The black solid residue was collected and washed with ethanol and distilled water, and dried at 60 °C in air. In addition, 500 mg of TiO<sub>2</sub> (P25) powder was annealed under NH<sub>3</sub> flow at 550 °C for 3 h as a reference sample [22], which we denote as N-TiO<sub>2</sub>.

Pt/PHC-NFs (1.0 wt.%) and Pt/N-TiO<sub>2</sub> (1.0 wt.%) are prepared. Twenty milliliters of H<sub>2</sub>PtCl<sub>6</sub> (0.26 mM), and 100 mg of the as-prepared samples followed by sonication for 30 min and obtained a suspension. Then 10 ml of a solution containing 30 mg of NaBH<sub>4</sub> was added drop wise to the suspension, which was stirred at room temperature for 5 h. The suspension was then filtered to recover the solid product and washed copiously with water. The recovered solid was then dried in a vacuum oven at 60 °C for 24 h.

X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (D/max-III A, Japan) using Cu Kα radiation. The transmission electron microscopy (TEM) images were carried out on a JEOL-2010 TEM at an acceleration voltage of 200 kV. The chemical nature of C and N has been studied using X-ray photoelectron spectroscopy (XPS) in Kratos Axis Ultra DLD spectrometer with Al Kα X-ray (hν = 1486.6 eV) at 15 kV and 150 W. The binding energy was

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referenced to C1s line at 284.6 eV for calibration. FTIR absorption spectra were performed with a Nicolet FTIR-170SX spectrometer in the range of 500–4000  $\text{cm}^{-1}$  at room temperature, in transmission mode in a KBr pellet. Elemental analysis was taken on an Elementar Vario EL-III elemental analysis instrument. Raman spectra were recorded with a LABRAM-HR Confocal Laser MicroRaman Spectrometer. The TGA measurement was carried out under a stream of nitrogen at a heating rate of 10  $^{\circ}\text{C}/\text{min}$  with a Perkin-Elmer Diamond TG/DTA instrument. The Brunauer–Emmett–Teller (BET) surface area ( $S_{\text{BET}}$ ) was determined by nitrogen adsorption–desorption isotherm measurements at 77 K on a Micromeritics ASAP 2010 system. The samples were degassed in vacuum at 473 K until a pressure lower than  $10^{-6}$  Torr before the actual measurements.

The photocatalytic reaction was conducted in a 200 ml cylindrical glass vessel fixed in the XPA-II photochemical reactor. A 500 W Xe lamp was used as the simulated solar light source (UV–visible light), and a house-made filter was mounted on the lamp to eliminate infrared irradiation. The visible-light was obtained by using the cut-off filter. The cut-off filter was made up of 1 M sodium nitrite solution which can absorb the light with wavelength under 400 nm [23]. This solution was injected into the interlayer of the quartz cool trap and was placed behind the water filter to completely remove the UV portion of the radiation and to supply a visible-light source. MO with the concentration of 20 mg/l was used as contamination. In order to obtain an optimally dispersed system and reach complete adsorption/desorption equilibration, 20 mg photocatalyst powder dispersed in 200 ml reaction solutions by supersonic for 15 min and then the suspension was magnetically stirred in the dark for 1 h. During the photocatalytic reaction, air was blown into the reaction medium at a flow rate of 200 ml/min. At regular intervals, 8 ml of the suspension was filtered and then centrifuged. The concentration of the remaining MO was measured by its absorbance ( $A$ ) at 465 nm with a Hitachi UV-3010 spectrophotometer. The degradation ratio of MO can be calculated by  $X = (A_0 - A) / A_0 \times 100\%$ .

### 3. Results and discussion

The morphology of the as-prepared sample was examined with TEM. Fig. 1a, b and c shows the typical TEM images of the as-prepared samples. It can be seen that the nanofibers were formed. Fig. 1b shows that the as-prepared sample consists of porous nanofibers. Their length and outer width are about 1–2  $\mu\text{m}$  and 100–250 nm, respectively. The HRTEM image (Fig. 1c) shows a disordered wall of the nanofibers, which agrees with the very weak diffuse ring of ED patterns (inset).

The result of FTIR spectrum (Fig. 1d) shows that the as-obtained sample resembles the  $(\text{HCN})_x$  polymer [10]. The infrared absorption spectrum shows a broad band between 1670 and 1050  $\text{cm}^{-1}$  with a peak at 1635  $\text{cm}^{-1}$  attributable to imine chains  $-\text{C}=\text{N}-$  and other

two sub-bands at 1383 and 1257  $\text{cm}^{-1}$  which were also observed in  $(\text{HCN})_x$  prepared directly from HCN [8–10,24]. No evidence of the  $\nu_{\text{C}=\text{N}}$  stretching band at 2200  $\text{cm}^{-1}$  [8–10,24]. Another feature of the polymer obtained from thermal treatment of formamide is the broad infrared absorption band between 3150 and 3400  $\text{cm}^{-1}$  attributed to amine N–H stretching. Instead,  $(\text{HCN})_x$  obtained by bulk and anhydrous polymerization shows an elemental analysis completely in line with the theoretical expectation of  $(\text{HCN})_x$  and a strong  $\nu_{\text{C}=\text{N}}$  stretching [8–10,24]. The infrared spectrum of Fig. 1d shows that the polymer from formamide is more similar to the  $(\text{HCN})_x$  polymerized in water because of the absence of the  $\nu_{\text{C}=\text{N}}$  stretching. Compared with FTIR spectra before reaction, the FTIR spectra have no significant changes after photocatalytic reaction, which indicates that the photocatalyst has stability. The elemental analysis of the black residue shows an elemental composition of C: 47.2%, H: 3.00%, N: 38.4% and O: 11.4%. The result shows that the C/N the ratio of as-prepared nanofibers is 1.23.

Fig. 2 shows the XPS spectrum of the as-prepared sample. It indicates that the sample is mostly composed of carbon and nitrogen elements, as well as a residual amount of oxygen from the surface absorption. The N1s spectra in Fig. 2b show two peaks centered at 398.4 and 399.7 eV, which can be attributed to the C=N and C-NH<sub>2</sub>, respectively [10,24]. The C1s spectra in Fig. 2c can be deconvoluted into three peaks with binding energies of 284.61, 286.02, and 287.9 eV [10,24], which are assigned to C–C, C–N and C=N bonds, respectively. TGA and DTG results in Fig. 2d show the weight loss of the black residue during the calcination under nitrogen atmosphere. The DTG analysis displays several weight-loss peaks, with the fastest weight loss rate at 115  $^{\circ}\text{C}$ , which is ascribed to the removal of physically adsorbed water and ethanol. The TGA curve in the temperature range of 30 to 700  $^{\circ}\text{C}$  shows a total weight loss of 45 wt.%. The weight loss may be due to the unreacted residual of catalyst surface groups after 115  $^{\circ}\text{C}$ . Porous structure of the samples was characterized by nitrogen adsorption–desorption measurements. The isotherm and Barrett–Joyner–Halenda pore size distribution of PHC-NFs are shown in Fig. 2e and f. It is true that its desorption isotherm is type IV, which indicates mesoporous structures of the samples [25,26]. Fig. 2f presents the pore size distribution of the sample, with the main peak at 28.3 nm of PHC-NFs. This result is consistent with the results of the TEM.

X-ray diffraction (XRD) patterns (Fig. 3a) reveal the graphite-like structure of the PHC-NFs, showing the typical interlayer stacking peaks corresponding to an interlayer distance of  $d = 0.330$  nm. The peaks are similar to the characteristic peaks of the (002) plane diffraction for the reported graphite-like carbon nitride ( $\text{g-C}_3\text{N}_4$ ) ( $d = 0.342$ , 0.321, or 0.328 nm) [3–5]. Typical Raman spectrum of the PHC-NFs, as shown in Fig. 3b, shows two broad peaks at about 1349 and 1533  $\text{cm}^{-1}$ , corresponding to the G (graphitic) and D (disorder) modes of graphite like carbon nitrides, respectively. Raman spectrum of the PHC-NFs

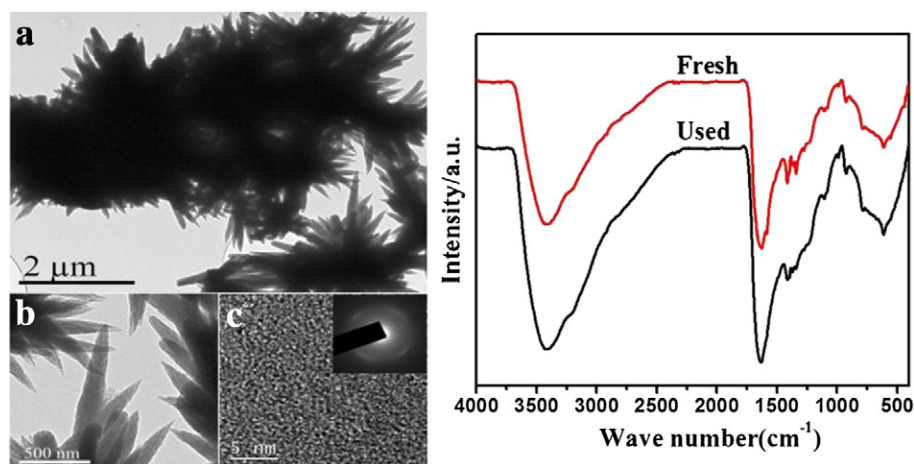


Fig. 1. (a) TEM, (b and c) HRTEM images of PHC-NFs (the inset is SAED spectrum), and (d) IR spectrum of as-prepared samples.

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