Enhancement of the graphitic carbon nitride surface properties from calcium salts as templates

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ABSTRACT

A graphitic carbon nitride material with enhanced surface properties has been successfully synthesized from guanidine monohydrochloride used as carbon nitride precursor, and from calcium salts nanoparticles used as templates. The products were characterized by X-ray Diffraction (XRD), chemical analysis, Fourier Transform Infra-Red spectroscopy (FTIR), nitrogen adsorption, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Ultra-Violet Visible spectroscopy (UV−Vis). The results show that the products adopt a graphitic structure with basal planes made of carbon and nitrogen atom species linked together by single and double bonds in an aromatic array (s-triazine, tri-s-triazine ring). As a function of the amount of the calcium-based template, a series of mesoporous materials was prepared which had specific surface areas ranging from 24.0 to 39.4 m^2/g and coupled with pore volumes of 0.13−0.22 cm^3/g. Instead of using the usual silica hard templates, our results show that using $CaCO_3$ and $Ca_3(PO_4)_2$ nanoparticles appears to be an encouraging solution for developing the surface properties of the carbon nitride. The carbon nitride is a promising candidate in the field of photocatalysis.

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1. Introduction

These days there is great interest in the graphitic carbon nitride, C_3N_4-g. This interest is thanks to its various properties that make it a reliable material with many potential applications in very different fields. Some of the advantages of the C_3N_4-g carbon nitride include its high thermal stability against oxidation in air (773 K), and its excellent chemical inertia toward both acid and alkali environment [1,2]. The electronic and optical properties of C_3N_4-g are also interesting. They include a small energy gap of 2.7 eV and a photoluminescence peak maximum at 420 nm, which can shift to higher values depending on the condensation degree and the packing between layers [3,4]. Among its potential applications, graphitic C_3N_4 seems to be appropriate as a gas storage material [5] and as a heterogeneous metal-free catalyst for Friedel−Crafts Reaction [6] or for NO decomposition [7]. More recently, its most recent potential and promising application is producing hydrogen by splitting water under visible-light irradiation [8]. Due to its smaller band gap, C_3N_4-g covers a wider spectrum that can be enlarged by specific doping [3].

Typically, carbon nitride powders are synthesized through the pyrolysis of carbon- and nitrogen-rich molecules (cyanamide, melamine, dicyandiamide, cyanuric species, guanidine salts) at relatively low temperatures (500−600 °C) [9−27]. These methods yield materials with low specific surface areas (<10 m^2/g) which limit using the materials in many potential applications in particular in the separation, selection and catalysis fields. There has been a lot of interest in enhancing the C_3N_4-g material's surface properties such as specific area, porosity and pore diameter, and many teams have published papers on classical uses of templates to prepare porous carbonaceous materials such as silica in the form of spheres [6,27] or matrices [17,22,28]. Zeolites (HZSM-5) [29], layered clays (saponite, montmorillonite) [30], and alumina porous coordination polymers [10] have also been employed successfully as hard templates. But in all these cases, using hydrofluoric acid (HF) or ammonium bifluoride (NH_4HF_2) is mandatory for template removal. We maintain that this point could hinder the industrialization of the processes. Few authors have suggested using soft

templates such as non-ionic surfactants and amphiphilic block polymers (Triton X-100, Pluronic P123 …) [14]. Proposing suitable (hard-) templates is a real scientific and industrial challenge for it is hard to scale up the production of these materials that exhibit tailored surface properties.

The present paper reports the synthesis of a graphitic carbon nitride material with enhanced surface properties obtained from pyrolysis of guanidine monohydrochloride (Gu·HCl) and nano-sized calcium carbonate (CaCO$_3$-nm) and calcium phosphate (Ca$_3$(PO$_4$)$_2$-nm) particles used as g-C$_3$N$_4$ molecule precursor and as hard template agents, respectively. The main advantages of the calcium minerals are their low cost, their nanoscale (10−100 nm), commercial availability and their low chemical resistivity against diluted mineral acid (hydrochloric acid). Calcium carbonate has already been used successfully for generating mesoporous carbon, silicalite, titania and polymeric carbon nitride [31−35] and we find that it can act as a suitable template. In opposite to the work of Wang et al. [35], we used in our investigation nanosized calcium carbonate particles as template which should allow the prepara-tion of carbon nitride materials with higher surface properties as observed with the use of silica spheres templates of 12 and 290 nm, respectively [6,27]. Calcium phosphate, to your knowl-edge, has never been suggested as template for the synthesis of enhanced surface properties ceramics. Pristine products have been identified and characterized by various techniques, as described below.

2. Experimental section

Guanidine hydrochloride (Gu.HCl, CH$_6$N$_3$Cl, NH$_2$(=CH)NH$_2$·HCl, 99%) was purchased from Alfa Aesar. Calcium carbonate (CaCO$_3$, 97.5%) and calcium phosphate (Ca$_3$(PO$_4$)$_2$, 98%) hard nanotemplates were supplied by SkySpring Nanomaterials Inc. Hydrochloric acid (HCl, 37 wt %) was purchased from Prolabo. All the reagents were used without further purification.

2.1. Synthesis of the graphitic carbon nitride material

Typically, synthesizing high specific surface area graphitic carbon nitride powders occurred as follows: 4.00 g of Gu·HCl was dissolved in 30 mL of ethanol solution. 0.5 g and 1 g of calcium carbonate nanoparticles or 0.25 and 0.5 g of calcium phosphate nanoparticles were added to the solution obtained, and the resulting dispersions were magnetically stirred and sonicated for 30 min. The solvent was evaporated at room tem-perature until white powders were obtained. The powders were ground in a mortar, placed in a quartz crucible, and heat-treated under argon atmosphere (100 mL/min) with a heating rate of 5 °C min^{-1} up to 550 °C (3 h). During the experiments, ammonia gas (NH$_3$) was released. The resulting monoliths were ground and washed with diluted hydrochloric acid (0.1 M−100 mL) to remove the templates. The dispersions were centrifuged and the precipitates were washed with distilled water and also once with acetone. Finally, the powders were dried overnight in an oven at 100 °C. For clarity's sake, the different samples were termed as C$_3$N$_4$_CaC$_x$ and C$_3$N$_4$_CaP$_x$, where CaC and CaP symbolizes CaCO$_3$ and Ca$_3$(PO$_4$)$_2$, respectively and x their amount in the initial mixture. These terms do not reflect the exact chemical compo-sition of the as-prepared samples. To evaluate the influence of the template on the porosity development of the carbon nitride material, a reference sample (C$_3$N$_4$) was prepared under the experimental conditions described above, but without the use of template nanoparticles. In that case, the carbon nitride phase yield is ca. 25%.

2.2. Characterization

The X-ray powder Diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer (Cu-Kα radiation) equipped with a Lynxeye detector and operating at 40 kV - 40 mA. The analysis was performed in the range of 2? = 20−80° with a 2θ step size of 0.02°. A chemical analysis (C, N, H, O and Cl) of the carbon nitride material (reference) was performed by CNRS laboratories (Vernaison and Nancy, France). For this purpose, the sample was burned under pressure with a helium/oxygen flow at 1050 °C. The reaction products (CO$_2$, H$_2$O, NO$_x$ …) were separated on a chromatographic column and quantified by using a thermal conductivity detector. The Fourier Transform Infra-Red (FTIR) spectroscopic analysis of the samples was conducted by means of a Bruker Tensor 27 spec-trometer. The spectra were collected in the Attenuated Total Reflection (ATR) mode and recorded in the wavenumber range of 4000−520 cm^{-1} by superposing 15 scans. Nitrogen sorption mea-surements were carried out with a Micromeritics SA 2020 surface area analyzer on the samples (−196.15 °C), outgassed at 200 °C for 6 h under vacuum. The specific surface areas (S$_{BET}$) were deter-mined by using the Brunauer−Emmett−Teller (BET) method in the 0.05−0.25 relative pressure range. The pore size distributions were obtained by the Barrett−Joyner−Halenda (BJH) model from the desorption branch, whereas the total pore volumes (V$_p$) were estimated from the volume of nitrogen adsorbed at a relative pressure P/P$_0$ of 0.989. The morphology of the samples, previously sprayed with a 5-nm-thick layer of gold (Desk II TSC, Denton Vac-uum), was studied by Scanning Electron Microscopy (SEM) oper-ating at 10 kV with a Nova NanoSEM 450 microscope (FEI). The Ultraviolet−Visible (UV−Vis) diffuse reflection spectrum of the sample was recorded on a CARY 5E spectrophotometer (Varian) in the 300−800 nm range.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the carbon nitride material. It shows material prepared without and with different amounts of calcium salts nanoparticles (C$_3$N$_4$_CaC$_x$ and C$_3$N$_4$_CaP$_x$). As can be observed from the wide-angle PRD patterns, the nitrogen-based materials exhibit one obvious broad characteristic peak around 2Θ = 22−23° and another weaker peak around 2Θ = 13° (Fig. 1(a)). These peaks are respectively attributed to the
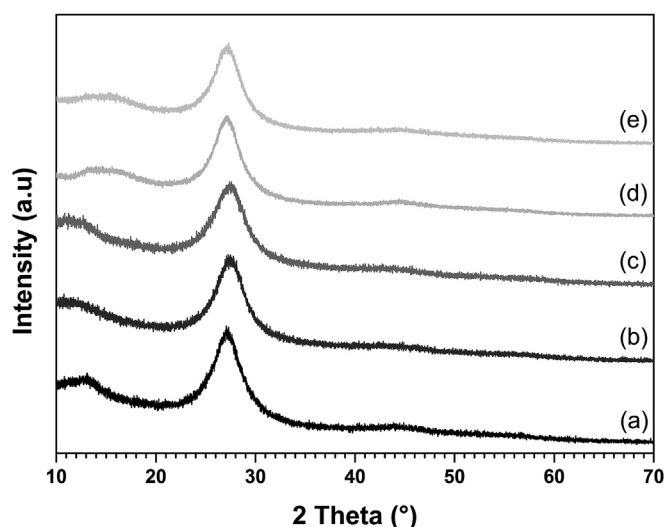

Fig. 1. X-ray diffraction patterns of C$_3$N$_4$ (a), C$_3$N$_4$_CaC$_{0.5}$ (b), C$_3$N$_4$_CaC$_1$ (c), C$_3$N$_4$_CaP$_{0.25}$ (d) and C$_3$N$_4$_CaP$_{0.5}$ (e).