



Arsenite remediation by an amine-rich graphitic carbon nitride synthesized by a novel low-temperature method

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HIGHLIGHTS

- Novel synthesis of graphitic carbon nitride through low temperature solvolysis.
- Surface Complexation Modeling reveals that GCN bears surfacial $-\text{NH}_2$ groups which are able to bind Cu(II) and As(III).
- GCN is a promising As(III) remediation-material thanks to its high As(III)-uptake-capacity (39.7 mg g^{-1}).
- EPR spectroscopy reveals that GCN is able to transfer electrons to adsorbed electron acceptors.

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ABSTRACT

A novel graphitic carbon nitride (GCN) material has been synthesized through a low-temperature solvolysis of sodium cyanide in formamide. The structure and morphology of the so-obtained GCN solid were studied by X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman/Infrared (IR) spectroscopy and thermal gravimetric analysis (TGA). GCN is characterized by a compacted layered structure bearing a high content of pendant amine groups (1.4 mmol g^{-1}). Electron Paramagnetic Resonance spectroscopy reveals that the pendant amine groups are readily accessible by extrinsic metal cations. Moreover, GCN has a considerable electron-donating capacity to adsorbed electron accepting ions such as Cu^{2+} . GCN shows an appreciable As(III) uptake capacity of 39.7 mg g^{-1} . Based on theoretical Surface Complexation Model we provide a consistent interfacial/structural picture that describes quantitatively observed phenomena.

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1. Introduction

Graphitic carbon nitride (or carbon nitride) is an important carbon-based layered material that, on account of its unique semiconductor properties, holds great promise in artificial photosynthesis [1], water splitting [2] and photocatalytic degradation of organic pollutants [3]. Moreover, by metal-inclusion carbon nitrides offer

advantages in the design of tunable photocatalysts through fine tuning of the band-gap of the parent semiconductor [4]. Although carbon nitride is considered as an emerging optical and catalytic material [4–7], its potential use towards toxic-metal removal from water has not yet been investigated (e.g. such as arsenic removal).

Arsenic is mobilized by natural weathering reactions, biological activity, geochemical reactions and other anthropogenic activities. Also, arsenic is known to be a toxic contaminant in drinking water, associated with adverse health effects, like chronic poisoning, dermatitis and cancer. Generally, arsenic in water may exist in trivalent As(III) or pentavalent As(V) states with As(III) (arsenite) being more toxic and with higher mobility than As(V) (arsenate)

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[8]. USA Environmental Protection Agency has set the As(III) limit in ground and drinking water at $0 \mu\text{g L}^{-1}$ [9]. Several materials have been proposed for arsenic removal from water based on zeolites, active carbons, magnetic iron/iron oxide nanoparticles and polymer fibers [10–13]. The adsorption efficiency of these materials depends on the molecular configuration and redox state of surface-functional groups, which should function efficiently via complexation or electrostatic interaction with arsenic. Various functional groups have been proposed as efficient arsenic-binding sites, including carboxyl, hydroxyl, amide and amino groups. Among them, the amino group has been found to be one of the most efficient chelates for arsenic adsorption from aqueous solutions [13–17].

So far, most of the reported synthetic methods used to prepare carbon nitrides require high temperatures. This results in formation of fully condensed networks with only few amine group functionalities remaining in the solid. Such materials are expected to have poor adsorption capacity towards arsenic e.g. due to low-content of amine groups on their surfaces. Accordingly, synthesis at lower temperatures is necessary in order to obtain partly condensed carbon nitrides with relatively more pendant amine groups. To this aim, we describe here the synthesis of amine-rich carbon nitrides based on the solvolysis of sodium cyanide in formamide. The material (Graphitic Carbon Nitride herein called GCN) bears a high amount of surface-accessible NH_2 groups and, thanks to this, it displays good arsenite adsorption capacity (39.7 mg g^{-1}) at pH 7. The synthesis, characterization and arsenite uptake of the carbon nitride sorbent are discussed below.

2. Materials and methods

2.1. Synthesis and reagents

2 g NaCN (Aldrich) were dissolved in 50 mL formamide (Aldrich) under stirring (30 min) at room temperature (25°C). The transparent solution was refluxed for 20 h under stirring to afford a brown precipitate. The precipitate was isolated by centrifugation at 5000 rpm for 10 min and then washed 6 times with deionized water ($6 \times 50 \text{ mL}$) and 2 times with acetone ($2 \times 50 \text{ mL}$), each washing step followed by centrifugation as above. The brown solid (herein codenamed GCN) was finally dried at ambient conditions ($T = 25^\circ\text{C}$). Yield: 2 g. GCN is stable in water or organic solvents. However, it is readily soluble in concentrated HCl resulting in a deep-brown colloidal dispersion. Similar acid solubilization has been also observed for highly crystalline carbon nitride [7].

2.2. Characterization techniques

GCN was characterized by powder X-ray diffraction (XRD) on a PANalytical X'PertPRO diffractometer using $\text{CoK}\alpha$ radiation, equipped with an X'Celerator detector. TEM images were obtained on a JEOL JEM 2010 microscope (LaB6 cathode). TGA traces were obtained under air with a Perkin–Elmer Pyris TGA/DTA instrument at a heating rate of $10^\circ\text{C min}^{-1}$. Elemental analyses (C, H, N, O) were obtained using a Perkin–Elmer Series II 2400 elemental analyzer. The N_2 adsorption–desorption isotherms were measured at 77 K on a Sorptomatic 1990, Thermo Finnigan porosimeter. The sample was outgassed at 120°C for 20 h under vacuum ($10\text{--}4 \text{ mbar}$) before the measurements. Specific surface area S_{BET} was determined with the Brunauer–Emmett–Teller (BET) method using adsorption data points in the relative pressure P/P_0 range 0.01–0.30. Raman spectra were recorded using a Raman microscope system (Renishaw, System 1000) consisting of an optical microscope (Leica) coupled to a Raman spectrometer. Infrared spectra

were recorded in KBr pellets with a FT-IR spectrometer of Bruker, Equinox 55/S 123 model.

2.3. Potentiometric titrations

The H-binding profile of the GCN solid has been measured by potentiometric base titration. 26 mg of material were suspended in a titration cell (Metrohm) containing 13 mL of Milli-Q water to yield a concentration of 2 g L^{-1} . The suspension was purged with 99.999% N_2 gas for 20 min before titration and then titrated with a 12.2 mM NaOH solution using an automatic Metrohm 794 Basic Titrino burette. pH was measured with a Metrohm Pt-glass electrode (6.0262.100). For the theoretical analysis, the FITEQL 4.0 software [18] was used to determine the best fit of surface complexation reactions, to the experimental data. The present data could be successfully fitted assuming that the observed H-binding is due to four types of molecular groups with a narrow distribution of pK_a values. The amount of these sites and the relative dissociation constants (pK_a) were the fitting parameters of the experimental H-binding titration.

2.4. Electron Paramagnetic Resonance (EPR) spectroscopy

Electron Paramagnetic Resonance (EPR) spectra were recorded with a Bruker ER200D spectrometer at liquid nitrogen (77 K) temperatures, equipped with an Agilent 5310A frequency counter. The spectrometer run under a home-made software based on Lab-View [19]. Adequate signal to noise was obtained after 5–10 scans. In case of powder samples, 5 mg of the material was inserted in a quartz EPR tube (Suprasil, Willmad Glass) with an outer diameter of 5 mm. Spin quantitation was done using 2,2-diphenyl-1-picrylhydrazyl (DPPH) as spin standard. Quantification of adsorbed Cu^{2+} ions was done using a CuCl_2 ($\geq 99.995\%$) anhydrous powder from Sigma–Aldrich, as spin standard. All EPR spectra were simulated by EasySpin 4.5.1 software package [20], implemented in MATLAB (Mathworks, Inc.).

2.5. Analytical determination of As(III)

The concentration of As in aqueous solution was determined by Cathodic Stripping Voltammetry (CSV) using a Trace Master5-MD150 polarograph by Radiometer Analytica. CSV is well suited for analytical determination of As(III) [21] with a detection limit, in our set up, of $0.5 \mu\text{g L}^{-1}$. The measuring cells were borosilicate glass cells, obtained from Radiometer. The working electrode was a hanging mercury drop electrode (HMDE) with drop diameter of 0.4 mm generated by a $70 \mu\text{m}$ capillary. An Ag/AgCl electrode with a double liquid junction was used as the reference electrode whilst a Pt electrode was used as a measuring electrode. Importantly, samples were not purged with N_2 gas e.g. in order to avoid loss of As(III) [21]. During the stripping step the solution was stirred at 525 rpm. For the measurements we used aliquots of 8.3 mL, adjusted at pH 0.5 with HCl [22]. Then, 8 ppm Cu^{2+} was added and the pH was readjusted if necessary to pH 1.5. In the following, As(III) was determined by square-wave CSV (SW-CSV) with accumulation potential $E = -400 \text{ mV}$ and accumulation time 60 s. As(III) was quantified by its signal at $E_{1/2} = -670 \text{ mV}$.

2.6. As(III) adsorption experiments

As(III) uptake from aqueous solutions was studied in batch experiments. Adsorption kinetics of arsenite onto GCN, were screened for contact times ranging between 0 and 240 min at pH 7, $\text{NaAsO}_2 = 3 \text{ mg L}^{-1}$, $\text{GCN} = 0.5 \text{ g L}^{-1}$. In each experiment the supernatant was collected by centrifugation and then analyzed for arsenite.

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