A NOVEL ROUTE OF SYNTHESIS OF SULPHUR-DOPED G-C$_3$N$_4$

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Abstract

A novel two-step pathway towards sulphur-doped graphitic carbon nitride (CN) was hypothesized and practically tested. As a result of that, three new materials with the different content of sulphur (up to 0.023 wt.%) were synthesized. These materials were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRFS), Fourier transform infrared (FTIR) and Raman spectroscopy and UV-Vis diffuse reflectance spectroscopy (DRS) all of which were compared with materials coming from procedures known in literature. Furthermore, photocatalytic properties of gained materials towards the decomposition of acid orange 7 (AO7) were tested and compared to known materials as well. All of three materials show less S-enrichment than CN (SCN) obtained by established procedures from thiourea, on the other hand, they bear a remarkable photocatalytic properties in photodegradation of AO7.

Keywords: Catalysis, graphitic carbon nitride

1. INTRODUCTION

Doped graphitic carbon nitrides have attracted an attention of researchers in past decade for several of their remarkable shifts in physico-chemical properties tuning already interesting properties of g-C$_3$N$_4$ itself. Superior photocatalytic properties of doped CN have attracted a lot of attention [1-3]. Non-metallic elements having accessible d-orbitals, such as sulphur and phosphorus are known to tailor electronic, Lewis and Brønsted acidobasic as well as photonic and optoelectronic properties of the material in favor of catalytic properties of the material [2]. Especially sulphur-doped CN catalysts were used multiple times in successful photodegradation of several organic dyes or model organic pollutants such as rhodamine [4], methyl blue [5], UO$_2^+$ dyes [6], bisphenol A [7] etc.

There are several methods of synthesis of SCN. The first set of methods in the pyrolysis of compounds containing sulphur, carbon and nitrogen in one molecule. Thiourea [5] is the most prolific example of such precursors. Despite remarkable results of such materials there is a lack of accordance about detailed structure of resulting S-enrichment of CN, moreover the possibilities of direction of such synthesis in favor of one particular kind of S-enrichment is very limited (there is still a lack of detailed knowledge which kind of the S-enrichment is beneficial to a target application). The other set of methods is combined pyrolysis of known CN (urea, cyanuric acid, melamine or dicyandiamide) precursors and sulphur containing compounds - sulphur precursors. The mixture of melamine and elemental sulphur (S$_8$) is known not to provide any SCN [8], only structurally altered CN is yielded. The interesting material is reported by co-polymetration of melamine and trithiocyanuric acid which is believed to be a sort of S-doped CN [4]. On the other hand, the aforementioned method suffers for the similar shortcomings as the thiourea pyrolysis.

With this knowledge, we decided to investigate a novel strategy to gain S-doped CN. We hypothesized that the pre-treatment of melamine with a reactive sulphur-containing compound may yield a chemical complex or

mixture of compounds with pre-made bonds between CN-precursors (melamine) and sulphur dopants. In our abstraction, it would increase the chance of sulphur to end up in the structure of a resulting material. As the dopant, the compounds consisting mostly of sulphur and nitrogen were sought. Hydrogen and oxygen were taken into account as elements whose presence in the dopant is possible, metallic salts of all kind were avoided due to the concerns of possible yielding combined metal-sulphur doped materials. Considering these conditions ammonium polysulphide ($(NH_4)_2S_x$) was chosen as i) meeting all of the conditions mentioned above and ii) being a N- and S-containing compound not often considered as a sulphur dopant for such materials.

In this contribution we describe the results of our initial experiments with potentially sulphur-doped graphitic carbon nitride coming from the two-step process using $(NH_4)_2S_x$ as a pre-pyrolysis agent and source of sulphur. The resulting materials were characterized and the screening for the photocatalytic properties of them was carried out.

2. EXPERIMENTAL

A two-step process was used to prepare the S-doped CN (S_xCN) materials. The first step consists of preparation of precursors, a powder mixture of ammonium polysulfide and melamine (section 2.1.). The second step consists of pyrolysis of precursors in a furnace (section 2.2). The methods of characterization of resulting materials are provided in section 2.3. and an initial assessment of their photocatalytic properties was made by a reaction of AO7 and is described in section 2.4. All of the measurements were compared with CN and SCN.

2.1. Precursors preparation

Ammonium polysulfide (25% aqueous solution, Fluka) and melamine (Aldrich) were purchased from particular vendors and used without further adjustment. All used chemicals were of analytical-reagent grade.

In a typical procedure, melamine (10 g; 79 mmol) was placed in a 250 ml beaker containing a stirring bar located in an oil bath on the hotplate of a magnetic stirrer. The solution of ammonium polysulfide (1 ml, 10 ml and 100 ml) was added to a mixture portion-wise (in dependence on the amount of ammonium polysulfide). Such obtained mixture was heated up to 120 °C (oil bath temperature), while vigorously stirred, until a yellow powder (precursor) was formed. Reaction mixture tended to heat itself spontaneously and obviously gasses of a smell of hydrogen sulfide have been formed during the course of the reaction. Resulting precursors were labeled according to portions of both substrates as [1:10]P for those coming from 1 ml of polysulfide and 10 g of melamine, respectively, [10:10]P coming from 10 ml of polysulfide and 10 g of melamine and [10:1]P (coming from 100 ml of polysulfide). They were used in a next step (section 2.2) without further adjustment or analyses.

2.2. Synthesis of materials

Precursors [1:10]P, [10:10]P and [10:1]P were placed in a ceramic crucible with a lid and heated in a furnace up to 550 °C (onset 3 °C.min-1, duration 4 hours). After the pyrolysis period, samples were removed from the furnace and left to cool to an ambient temperature. The resulting materials were grounded in a mortar to a neat powder. Such gained photocatalysts were labelled SxCN-A (coming from [1:10]P), SxCN-B (coming from [10:10]P) and SxCN-C (coming from [10:1]P) and submitted for characterization and tested on photocatalysis. Samples CN and SCN were prepared by a calcination of 10 g of a precursor (CN - melamine, SCN - thiourea) under same conditions as mentioned above for SxCN samples.

2.3. Characterization of photocatalysts

The photocatalysts S_xCN-A, S_xCN-B and S_xCN-C were characterized by X-ray powder diffraction, infrared spectroscopy, and Raman spectroscopy. The sulphur content was determined by X-ray fluorescence spectroscopy. Photonic properties were determined by diffuse reflectance spectroscopy.

XRD patterns were recorded on diffractometer Miniflex 600 (Rigaku) equipped with Co tube and 1D detector D-Tex and were carried out in a range 10 - 90 °2Theta. The crystallite size was calculated using Scherrer's equation

$$L = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \qquad (1)$$

where L is the crystallite size (nm), λ is the wavelength of the X-rays (0.17889 nm), β is the peak width in the half of maximum height of given diffraction peak (rad), K is the constant related to the crystallite shape (0.9), θ is the Bragg's angle (rad or degree).

UV-Vis diffuse reflectance spectra were recorded with a Shimadzu UV-2600 (IRS-2600Plus) spectrophotometer at room temperature in a range of 220-800 nm.

The IR spectra were collected by a Fourier transform infrared spectrometer Nexus 470 (ThermoScientific, USA) with a DTGS detector using KBr pellets technique. Exactly 1.0 mg of sample was grounded with 200 mg of dried KBr. Pellets were pressed with a pressure corresponding to 8 tons for 30 seconds under vacuum. The measurement parameters were following: a spectral region 4000-400 cm^{-1}, a spectral resolution 4 cm^{-1}; 64 scans; and Happ-Genzel apodization. The treatment of spectra: polynomial (second order) baseline, subtraction spectrum of pure KBr.

The Raman spectra were measured at a dispersive Raman spectrometer DXR SmartRaman (ThermoScientific, USA) with a CCD detector. A 180° degree sampling was used as a measurement technique of the Raman spectroscopy. The measurement parameters were as follow: the excitation laser 780 nm, a grating 400 lines/mm, an aperture 50 μm, exposure time 1 second, a number of exposures was 1000, a spectral region was 1800-50 cm^{-1}. An empty sample compartment was used for background measurements. The spectra were treated with fluorescence correction (6th order).

The XRFS sulphur content determination was made on a XEPOS energy dispersive spectrometer (Spectro, Germany). Samples were measured using plastic cell in protective atmosphere (He). A method calibration was made based on mixtures of g-C_3N_4 and thiourea (Lachema, Czech Republic).

2.4. Photocatalytic experiments

A photocatalytic decay of AO7 was selected. AO7 (for microscopy (Hist.); Sigma-Aldrich) was diluted in demineralized water (purified on Aqual® 25 reverse osmosis column) to concentration 25 mg.l^{-1} and this solution (150 ml) was put into a vessel. Under dark conditions, 10 mg of each photocatalyst was added. After taking the intial samples (taken in τ_0) a lamp (368 nm, 0.94 mW.cm^{-2}) was turned on and reaction was let to proceed while stirring. Samples of 2 ml were taken each 20 min up to the time of 120 min. All of the samples, including the τ_0 ones were measured on UV spectrometer (ThermoSpectronic, Heλiosε) at the wavelength 485 nm (absorption maximum of AO7).

3. RESULTS AND DISCUSSION

The section 3.1. deals with the results of solid state analyses of S_xCN-A, S_xCN-B and S_xCN-C section 3.1. The following section 3.2. summarizes the results of the catalytic experiments and observed photocatalytic behavior of the materials. Comparison with known materials CN and SCN is also provided.

3.1. Characterization of photocatalysts

XRD patterns and crystallite sizes (**Figure 1**, **Table 1**) suggest the crystal structure of S_xCN-A, S_xCN-B and S_xCN-C is basically similar as both the CN and SCN. The 002 reflection (2θ = 32°) connected to g-C_3N_4-like materials is clearly visible in both samples and standard CN and SCN. Crystallite sizes suggest new materials

seem to have closer to the CN (7.0 nm) than to SCN (4.9 nm). This is in accordance with the XRFS determination of sulphur content. A content of sulphur in the S_xCN-A and S_xCN-B was below detection limit of 0.0002 %, which means the materials had no or very insignificant sulphur doping. The S_xCN-C on the other hand showed higher amount of sulphur (0.023 %), which is still one order less than in SCN (0.22 %). Similar information is provided by both IR and Raman spectra where the spectra (S)CNs and S_xCNs (**Figure 2**) are virtually indistinguishable. Notable differences between S_xCN-A, S_xCN-B and S_xCN-C and CN cannot be seen also in the DRS spectra (**Figure 3** left) where curves of new samples and standard are overlapped within the margin of experimental error. Noticeably, the DRS spectrum of SCN is the only one showing a distinction. The similarity of optical behavior of materials may further be demonstrated by values of forbidden bandgap all of which lay between 2.62 eV and 2.67 eV (**Table 1**).
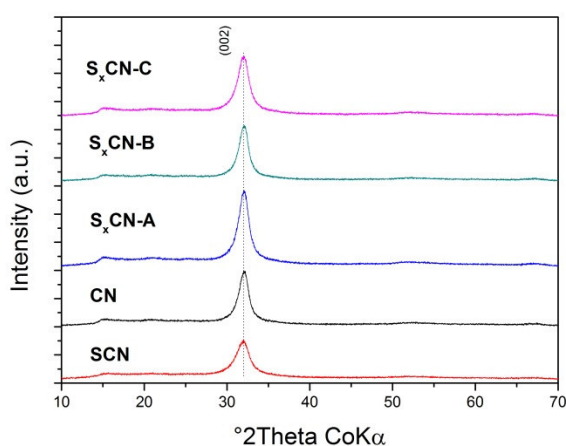

Figure 1 XRD patterns of prepared materials S_xCN-A, S_xCN-B and S_xCN-C, comparison with CN and SCN
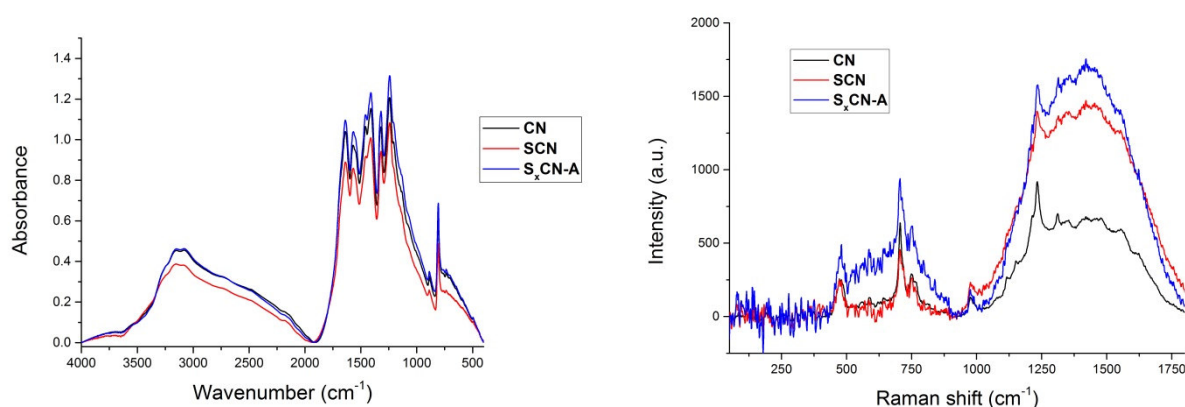

Figure 2 Comparison of IR absorbance (left) and Raman spectra (right) of CN, SCN and S_xCN-A

Table 1 Survey of measured properties of CN, SCN and S_xCNs, where L means crystallite size, E_g is energy of forbidden gap and S is content of sulphur

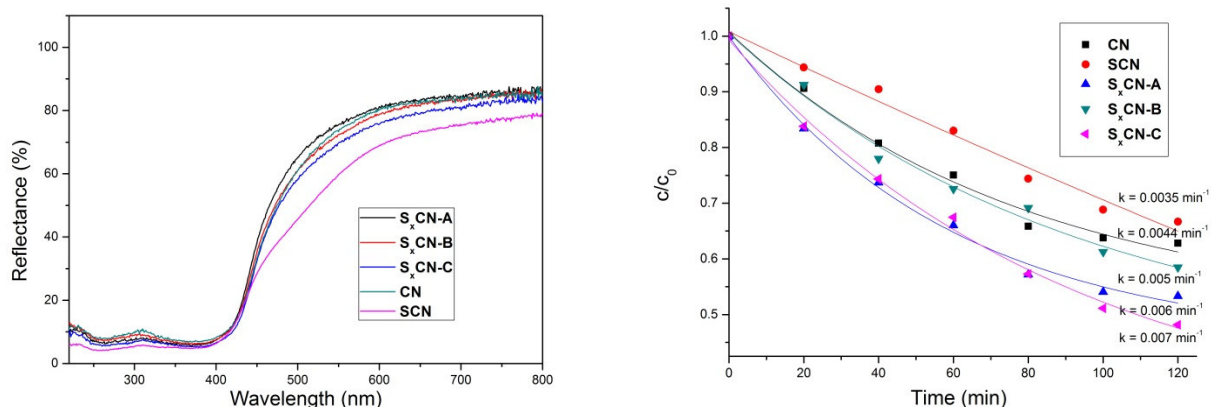| Material	CN	SCN	S_xCN-A	S_xCN-B	S_xCN-C
L (nm)	7.0	4.9	6.8	7.3	6.0
E_g (eV)	2.64	2.62	2.66	2.67	2.67
S (wt%)	< 0.0002	0.218	< 0.0002	< 0.0002	0.023

Figure 3 DRS spectra of prepared samples (S$_x$CN-A, S$_x$CN-B and S$_x$CN-C) and CN and SCN (left). The kinetic curves of photocatalytic experiments for the photocatalysts (right), where c and c$_0$ are the concentrations at time = t min and time = 0 min, respectively.

3.2. Photocatalytic properties

Both solid state analyses and DRS spectra draw a very blurred line between new materials and CN and SCN. Surprisingly, the photocatalytic behavior of S$_x$CN-A, S$_x$CN-B and S$_x$CN-C tells a different story. From **Figure 3** (right) showing the AO7 decomposition pattern under catalysis of both samples (CN and SCN) and new materials (S$_x$CN-A, S$_x$CN-B and S$_x$CN-C) a clear distinction can be made between the CN and SCN and new ones. A slight increase of the decomposition first order rate constants (6·10^{-3}min^{-1} for S$_x$CN-A and 7·10^{-3}min^{-1} for S$_x$CN-C vs. 3.5·10^{-3}min^{-1} for SCN and 4.4·10^{-3}min^{-1} for CN) can be viewed. The biggest distinctions are final conversions of AO7 after 2 hour where S$_x$CN-C (52 %), S$_x$CN-B (42 %) and S$_x$CN-A (47 %) conversions are significantly higher, than those of CN (37%) and SCN (33 %).

4. CONCLUSIONS

A novel method meant to be an alternative preparation of a new sulphur-doped CN yielded limitedly sulphur-doped material S$_x$CN-C. Though, all of three resulting materials S$_x$CN-A, S$_x$CN-B, S$_x$CN-C do exhibit an unusual photocatalytic behavior in the decomposition of AO7. The explanation may lay in similar altering of CN properties by its synthesis in flux of sulphur [8]. Either way, a detailed structure of new materials as well as a source of their outlaying photocatalytic properties will be a matter of our follow up works, which are currently underway.

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