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Baking ‘crumbly’ carbon nitrides with improved photocatalytic properties using ammonium chloride

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Ammonium chloride can serve as a green, unreactive and reusable template to prepare heptazine-based graphitic carbon nitrides with the surface areas up to 30 m^2/g and up to 6 times higher photocatalytic activity, by a simplified procedure that comprises *only* pyrolysis of the reaction mixture containing precursor and salt.

Carbon nitride materials with C_3N_4 approximate stoichiometry attract nowadays increasing attention as polymeric metal-free photocatalysts capable of full water splitting as it was first shown by X. Wang *et al*..[1] One of the still remaining challenges is the processing of these materials. Bulk carbon nitrides are obtained by heating a desired polymer precursor, e.g. cyanamide, dicyandiamide, or melamine to 550 °C,[2] and the resulting hard solid should be ground prior to any further characterization or application. Grinding is typically done manually, in order to avoid metal contaminations that inevitably accompany ball-milling, and it becomes time and efforts consuming if large quantities of the material have to be prepared. Alternative ways to increase surface areas of carbon nitrides include utilization of hard[3] and soft[4] templates during the synthesis. However, the former templates must be removed using toxic hydrogen fluoride sources, while the latter ones contaminate the resulting products with carbonaceous species making the products photocatalytically inactive. Recently, aluminum nitrate nonahydrate[5] and calcium carbonate[6] were suggested as green templates to prepare carbon nitride photocatalysts with the surface areas up to 90 and 40 m^2/g, respectively. However, the residues of the templates were to be removed during additional washing steps, so that it was not possible to recover and reuse the templates. Besides, the synthesis procedures were in both cases multistep. Therefore, it is still highly desirable to find a green and reusable template simultaneously enabling to reduce the number of carbon nitride preparation steps.

Here, we suggest ammonium chloride, which is actually used in baking to obtain crispy cookies, as a cheap, green, unreactive and reusable template to assist preparation of heptazine-based carbon nitrides with the increased surface areas. Ammonium chloride defines the morphology and texture of the products and causes development of macro-porosity in the solids. This leads to enhancement of the photocatalytic activity of the materials compared to the reference ground carbon nitride as exemplified by visible light driven Pt-assisted sacrificial water reduction reaction.

The products were obtained by dissolving the desired amounts of ammonium chloride and cyanamide in small amounts of water, drying the reaction mixtures and then pyrolysing them at 550 °C for 4 hours under a constant nitrogen flow. Alternatively, the reaction mixtures can be heated up without intermediate drying step that simplifies preparation procedure even further. Besides, water itself might act as a template.[7] Other carbon nitride precursors can be used as well. In order to reveal the influence of ammonium chloride onto the properties of final polymers, three different weight ratios of cyanamide to NH_4Cl, namely 1:2, 1:5 and 1:10, were used. The salt is quantitatively removed during the synthesis, eliminating the need to wash the products, so that the materials can be used as obtained after the heat-treatment (Table S1, ESI†). The reference bulk graphitic carbon nitride (further abbreviated as ref.-CN) was prepared by heating melamine to 550 °C under N_2 flow, holding at this temperature for 4 hours, cooling down and grinding the material to obtain fine powder.

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†Electronic Supplementary Information (ESI) available: description of the hydrogen evolution set up and measurement procedure; EA data, FTIR spectra, SEM images and N_2 sorption properties of the products; PXRD patterns and FTIR spectra of a sample product before and after HER. See DOI: 10.1039/x0xx00000x

In order to demonstrate the possibility to recover the template, the thermal condensation of cyanamide in the presence of NH_4Cl was carried out in a heated glass flask. The template was collected in a nearly quantitative yield of 98%. The experimental details, as well as characterization data of the recovered template are given in ESI (Table S2, Fig. S1, ESI†)

Ammonium chloride-derived materials as well as ref.-CN are characterized by the C/N weight ratio of ~0.58, regardless the amounts of the salt taken. The C/N weight ratios are lower than 0.64 expected for the C_3N_4 stoichiometry (Table S3, ESI†) due to the incomplete condensation and the presence of terminal amino-groups in all products, as suggested by the residual H content of ~ 2 wt.%. The products contain 3 to 5 wt.% oxygen that originates from the tiny amounts (3 ppmV) of oxygen gas in the nitrogen flow. The absence of chlorine in the NH_4Cl-materials suggests that the template was fully removed during the synthesis due to its decomposition.

PXRD investigations showed that the products obtained from ammonium chloride have the structure that is typical for ref.-CN (Fig. 1a).[1] Namely, the reflection at 2θ=27° represents the layer stacking motif while the diffraction peak at 2θ=13° is due to the in-plane periodicity of s-heptazine repeating units linked by tertiary nitrogen bridges. Compared to ref.-CN, NH_4Cl-derived polymers are slightly more disordered as follows from the lower intensities and broadening of the reflections in the corresponding PXRD patterns. Among NH_4Cl-products, the material prepared at 1:5 precursor to salt ratio is characterized by better structural order observed as higher intensity of the most pronounced reflection at 2θ=27°. Conversely, the solid prepared by direct heat-treatment of aqueous reaction mixture has the least ordered structure.

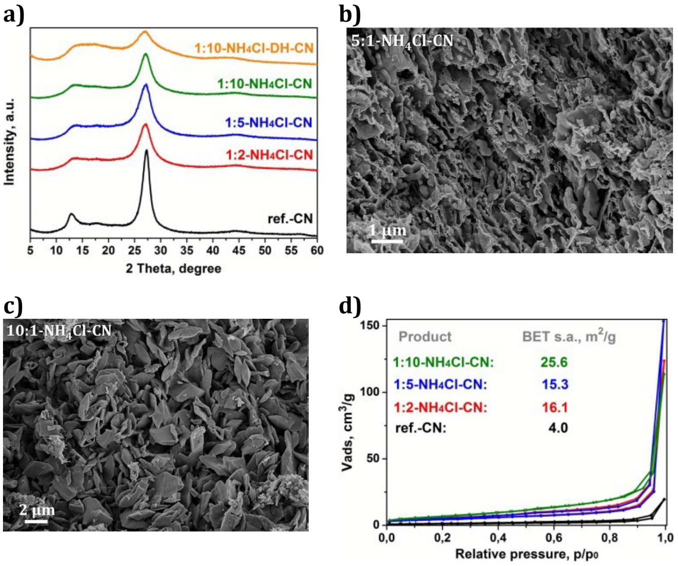

Fig. 1 PXRD patterns (a) and N_2 sorption isotherms (d) of the ref.-CN, and ammonium chloride derived products; SEM images of the solids prepared at 1:5 and 1:10 cyanamide to ammonium chloride ratios (b, c).

The FTIR-ATR spectra of the NH_4Cl-derived solids and ref.-CN are identical and composed of several characteristic bands (Fig. S2, ESI†). The main absorption band at 1100-1650 cm^{-1} is due to CN stretching and NH bending in the aromatic heterocycles.[8] The broad absorption band at 3000–3650 cm^{-1} suggests the presence of some surface hydroxyl groups, surface adsorbed water and terminal amino-groups, in agreement with EA data. The absorption band positions in NH_4Cl-derived products perfectly match those of the ref.-CN further confirming that ammonium chloride does not disturb the chemical structure of the target polymer.

The results of PXRD investigations are further reflected in the products particle morphology; and Fig. 1b, c and Fig. S3 a-c show the representative scanning electron microscopy (SEM) images of the solids prepared using different ratios of ammonium chloride to cyanamide and different precursors. Bulk carbon nitride (ref.-CN) has a dense layered structure, as shown in Fig. S3d. In general, ammonium chloride introduces cavities in between the layers providing carbon nitrides the morphology of layer cake, and disturbs the planarity of layers (see Fig. S3 e–i, ESI†). The BET surface areas of 1:2, 1:5 and 1:10 NH_4Cl-products are 16.1, 15.3 and 25.6 m^2/g, respectively, while ground ref.-CN has a surface area of 4.0 m^2/g (Fig. 1d). The gain in crystallinity by 1:5-product is accompanied by the consequent decrease of its surface area. The direct heating of the aqueous 1:10 reaction mixture to 550 °C delivers carbon nitride with the intermediate surface area of 16.9 m^2/g, as well as grinding of the selected precursor with ammonium chloride (Fig. S4, ESI†). As evident from the shape of nitrogen sorption isotherms of NH_4Cl-derived products (Fig. 1d), the template generates the external surface area and creates macroporosity in the products as indicated by the higher N_2 uptakes at relative pressures p/p_0 close to 1. The pore volume reaches maximum of 0.238 cm^3/g at $p/p_0=1$ when 1:5 cyanamide to ammonium chloride ratio is used.

Surface properties of photocatalysts are important to consider, since all reactions in heterogeneous photocatalysis start with the adsorption of the reagents on the catalyst's surface. Ammonium chloride upon decomposition produces hydrogen chloride and ammonia, and both can alter the surface states in the products. The influence of NH_4Cl on the surface properties of the resulting solids was accessed by Z-potentials measurements. The bulk ref.-CN has a Z-potential of –53.5±1.3 mV, while the corresponding values for 1:2, 1:5 and 1:10 NH_4Cl-derived materials are –50.2±0.9 mV, –51.4±0.9 mV and –49.0±0.1 mV, respectively. High negative charge at the surface can be explained by the surface hydroxyl groups (C-OH) that are highly acidic and dissociate in water to give surface $O^{\ominus}$ ions, as supported by EDS and FTIR studies. Thus, NH_4Cl-solids are characterized by less acidic surface than ref.-CN, probably reflecting the basicity of ammonia gas formed during template decomposition, but the difference is not that substantial to dramatically change the surface chemistry of the materials.

Optical absorption and emission properties of the polymers are compared with those of the ref.-CN in Fig. 2. All products show two absorption bands (Fig. 2a), the main one at λ < 410 nm and the minor one at λ ~ 500 nm that are due to $\pi \rightarrow \pi^*$ electron transitions in the conjugated aromatic ring system, and to $n \rightarrow \pi^*$ transitions involving lone pairs of the edge nitrogen atoms of the s-heptazine ring, respectively.[9]

Compared to ref.-CN, the solids prepared in NH_4Cl absorb significantly more visible light at 500 nm, and absorption at 500 nm is more pronounced in the case of 1:5-product. At the same time, optical band gaps of the products determined from the corresponding Tauc plots are very similar, between 2.72 and 2.77 eV. Thus, we assume that the bulk structure of the polymers is only little affected by the presence of ammonium chloride, which rather creates the defects at the surface of the materials. All NH_4Cl-products show significantly lower photoluminescence than ref.-CN (Fig. 2b). On one hand, this is partially due to the lower structural order (see Fig. 1a) in the obtained products resulting in greater energy losses at the lattice defects as explained below. Lower structural order implies the increased number of the lattice defects in a solid. Such lattice defects in the case of CN-polymers are reported to play the role of the deep level traps, at which the non-radiative recombination occurs.[10] Thus, as a result of the decreased crystallinity coupled to the increased number of the deep level traps, a lowering of PL intensity is observed. However, taking into account the high photocatalytic activity of the prepared solids (see below), this cannot be the only reason of the PL signals decrease. On the other hand, the decrease of PL intensity is the consequence of the improved charge separation in the prepared materials. In agreement with the absorption profiles, the emission spectra show two main peaks at ~470 nm and at ~530 nm. The product prepared at 1:5 cyanamide to ammonium chloride ratio is characterized by the lowest PL signal, which, taking into account its better structural order, clearly speaks for the improved charge separation in this solid.

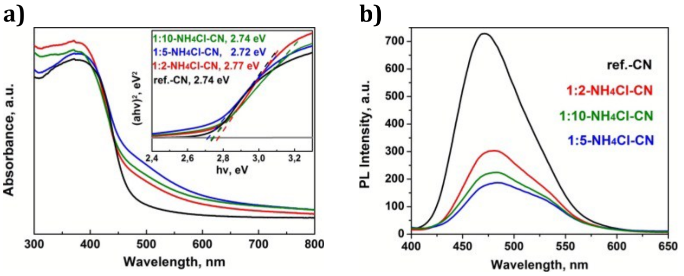

Fig. 2 UV-Visible absorption (a) and steady-state photoluminescence (b) spectra of the reference bulk carbon nitride and of the solids prepared using different amounts of NH_4Cl.

The photocatalytic activity of NH_4Cl-derived products was compared with the performance of ref.-CN in Pt-assisted sacrificial water reduction under irradiation with white light (50W LED). The experimental details are given in the Supporting Information, while the results of the tests are shown in Fig. 3. The NH_4Cl-solids show 3 to 6 times higher H_2 evolution rates compared to the reference ground ref.-CN which produces 0.66 µmol H_2/h (Fig. 3). The reaction rates increase with the increase of the surface areas of the photocatalysts used and reach 3.81 µmol H_2/h in the case of 1:10-NH_4Cl-sample having the surface area of 25.6 m^2/g. These findings suggest that the available surface area of the photocatalysts plays a more important role than their crystallinity in determining the activity of the solids in hydrogen evolution reaction (HER).

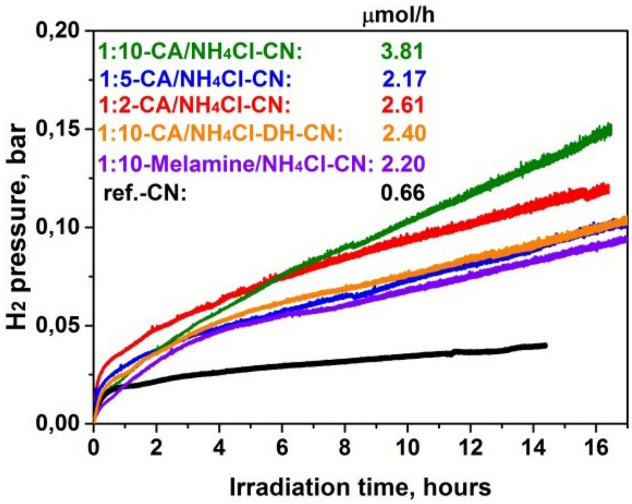

Fig. 3 The increase of hydrogen pressure as a function of irradiation time, using ref.-CN and NH_4Cl-products as photocatalysts, TEOA as a sacrificial agent, photodeposited Pt as a co-catalyst and 50W white light LED as an irradiation source.

The amounts of photodeposited Pt was found to be identical in both ref.-CN and 1:10-NH_4Cl-derived materials and equal to ~0.7 wt.%, thus excluding the possibility that the enhancement of the photocatalytic activity originates from higher amounts of the co-catalyst. The NH_4Cl-products are found to be stable during photocatalytic reactions as follows from identity of PXRD patterns and FTIR spectra of the most active 1:10-NH_4Cl-product before and after 17 hours of HER (Fig. S5, ESI†).

In summary, we used ammonium chloride as a template for preparation of heptazine-based carbon nitride polymers. Precursor condensation degree, chemical structure, structural order, absorption, emission and even surface properties of the target polymers are barely influenced by ammonium chloride. At the same time, NH_4Cl works as a template providing crumbly texture and higher surface areas to the products that fully eliminates the need to wash or grind them and results in up to 6 times increase of their photocatalytic activity in visible-light driven water reduction reaction. Besides, crystallinity, surface areas and morphology of the polymers can be tuned by selection of the specific carbon nitride precursor and by adjusting the precursor to ammonium chloride ratio. In this way, use of ammonium chloride enables facile and cheap preparation of large quantities of carbon nitrides. Potentially, this simple method can be further applied to other ammonium salts used in cooking, such as ammonium carbonate and ammonium sulphate, as well as to other carbon nitride precursors.

Acknowledgement

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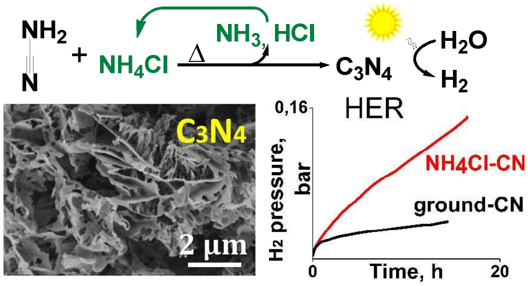

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