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Preparation and characterization of expanded g-C_3N_4 via rapid microwave-assisted synthesis

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ABSTRACT

Microwave assisted heating was successfully employed in significantly accelerated preparation of expanded g-C_3N_4 via thermal condensation of urea. Comparing to typical synthesis route, rapid microwave assisted heating enables not only shorten synthesis time from hours to few minutes but obtain reasonable yield of the product also. Use of ceramic kiln "hotpot" with intern covered with absorbing layer plays the key role in transformation of the microwave energy into heat. Heat energy in form of radiation from the glowing inner layer surface is focused into the internal volume of the kiln resulting in extremely fast temperature increase. Thus, microwave non-absorbing starting material is extremely fast heated. The effects of reaction conditions on the structural, morphological, optical and photocatalytic properties of prepared g-C_3N_4 were investigated in detail. Having similar specific surface area but much larger particles than its conventionally prepared analogue, the microwave prepared material can be classified as expanded g-C_3N_4. Moreover, by simply changing the reaction time, photoluminescence emission of the material can be continuously tuned covering the blue to green light region of visible light. The photocatalytic degradation of Methyl Violet 2B reveal that the adsorption capacity of samples increases with processing time while the rate constant slightly decreases. It can be ascribed to the expansion of the internal surface which results in its worse availability to the diffusion transport of the dye to active sites. It also impedes photodegradation products removal. The synthesis technique described here could be considered applicable to starting materials, which cannot be sufficiently heated by microwave absorption directly.

1. Introduction

Although being one of the oldest synthesized polymeric material, graphitic carbon nitride (g-C_3N_4) has regained significant interest after the demonstration of its utilization in hydrogen production from water under visible light by Wang et al. in 2008 [1]. Similarly to graphite, g-C_3N_4 possesses a stacked 2D structure, which can be regarded as nitrogen heteroatom substituted graphite framework consisting of π-conjugated graphitic planes formed via sp^2 hybridization of carbon and nitrogen atoms. The π-orbitals between single layers give rise to van der Waals interactions, imparting thus g-C_3N_4 an excellent thermal and chemical stability which, together with appropriate electronic structure (bandgap E_g ~2.7 eV), makes it suitable material for application in heterogeneous catalysis, photocatalytic decomposition of pollutants, LED devices, photo-electrochemical cells, bioimaging, etc. [2–11]. Among the most recent attempts to utilize g-C_3N_4, photofixation of nitrogen N_2 from atmospheric into NH_4^+ in electrolyte solution relies on the detailed material design, namely controlling of the concentration of nitrogen vacancies together with other complex of structural, microphysical and morphological properties. Nitrogen vacancies not only serve as active sites for adsorbing and activation of N_2 molecules but also promote interfacial charge transfer from catalysts to N_2 molecules resulting in significant improvement of nitrogen photofixation ability [12]. Last but not least, in contrast to conventional photocatalysts, g-C_3N_4 is a metal-free compound composed of carbon and nitrogen solely which are abundant in earth in many available forms, inexpensive and safe. In this respect, this material also goes hand in hand with demand for sustainable or green chemistry and reduction of environmental impact.

The synthesis of g-C_3N_4 is rather challenging task and many experimental approaches have been adopted to prepare well-defined carbon nitride structures as documented in many reviews [13–16]. Liquid-based approaches allow preparation of variety of g-C_3N_4 nanostructures by shaping, nanocasting and/or replication with high degree crystallinity and large surface area, but they suffer from long reaction times, etching of template, and often involve utilization of toxic

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chemicals [17–21]. In fact, the vast majority of methods used for g-C_3N_4 preparation are based on bulk reaction of oxygen free compounds containing pre-formed C—N core structures [22]. The most common synthesis routes involve solid state reaction between cyanuric chloride and/or, calcium cyanide [23], lithium azide [24], or melamine [25]. More recently, thermal condensation of single precursors such as cyanamide [26], dicyanamide [27], melamine [28], thiourea [29] or urea [30] have been proposed as facile methods for preparation of high quality g-C_3N_4. Among these precursors, urea is the most used material, yielding well crystallized product in the temperature interval of 450–550 °C with reaction time usually ranging from 2 to 4 h, either in self-supporting gas or inert atmosphere [30,31]. Because of long reaction time and relatively high temperature needed in conventional synthesis in a muffle furnace, microwave-assisted heating has been explored in order to shorten synthesis time and save energy. MW-assisted heating is well established group of techniques for rapid heating of reaction systems in both organic and inorganic chemistry in various typical instrumentation setups; however, microwave absorbing material or medium is prerequisite [32,33]. Although highly polar compound, urea itself does not absorb microwaves efficiently at the 2.45 GHz frequency. Microwave assisted pyrolysis of urea supported on graphite under solvent-free conditions was reported to overcome this problem and obtain condensed heterocyclic products [34]. Since cyanuric acid is the main intermediate involved in urea pyrolysis [35] the choice of more structurally complex precursors is one possibility how to improve the synthesis. For example, melamine structure is considered as more suitable than urea for transformation into graphene like product due to inherently present in plane C_3N_4 structural motive. However, melamine is a weak absorber also, therefore its mixtures with graphite [36] or carbon fibers [37] as best MW frequency coupling materials were employed to overcome this obstacle. On the other hand, it is difficult to separate carbonaceous supportive material from prepared g-C_3N_4 after synthesis and this approach as such is suitable rather for fabrication of composite materials than for obtaining pure g-C_3N_4. Consequently, few authors utilized reaction crucible capped with a lid buried in MW absorbing powder from CuO or SiC to heat the crucible efficiently while avoiding contamination of starting chemicals with absorbing material [12,38].

Herein we report a procedure for green synthesis of g-C_3N_4 material in terms of energy and time savings with potential to scale up product by using microwave-assisted solvent free heating of urea which allows for preparation of g-C_3N_4 within a few minutes. In contrast to previous works, we introduce another heating mechanism of the material. Utilization of the radiation energy transfer into the sample is different from approaches available in literature. It is expected that rapid heating enables preparation of expanded material, in comparison with conventionally prepared one, similarly as reported for expanded graphene [39,40] or vermiculite [41]. Moreover, simple changing of reaction conditions should enable tuning of final optical properties of obtained materials. Optical properties of these materials exhibit a wide spectral range of luminescence emission from the blue to green visible light region, extending the potential application of purely g-C_3N_4 in multi-colour-emitting devices. Up to this date, white emission has been observed on hybrid g-C_3N_4/ZnO material only [42]. Once g-C_3N_4 prepared, besides other methods, the surface properties of synthesized samples have been evaluated by adsorption of Methyl Violet 2B and photocatalytic properties of the material tested by degradation of this dye under UV irradiation.

2. Experimental

Graphitic carbon nitride was prepared by a thermal treatment of urea in self-supporting gas atmosphere. An alumina crucible containing 5 g of urea was covered by a lid and placed into a ceramic kiln (hotpot) equipped with a microwave absorbing layer. Through this thin layer, the energy of high-frequency alternating electric field in the cavity of a common household microwave oven (Hyundai, MWM 1417 W) was dissipated and the internal of the kiln including the crucible and the sample was extremely fast heated. The oven was operated at 750 W for 11–15 min with 1 min steps. The final maximum temperature achieved was monitored by an infrared contactless thermometer after switching off the microwave oven. Afterwards, the kiln was taken out of microwave cavity and left to cool down naturally. Samples were labeled according to the synthesis time 11–16 min as MW11–16 which correspond to the final maximum temperature inside the ceramic kiln ranging from 480 to 560 °C. It should be noted, that the temperature of absorbing layer was much higher during operation of microwaves as a red-orange glow was observed which corresponds to a temperature above 900 °C. The yield of these synthesis was 4 to 5% with respect to theoretical mass of the product calculated from initial source compound load assuming ideal stoichiometry. There was no observable trend of the yield dependence on synthesis time but the sudden total decomposition experienced for times longer than 16 min. For comparison with a conventionally produced material, a reference sample was prepared in Muffle furnace with a heating rate of 10 °C/min and then held at temperature of 550° for 3 h. The reference sample is labeled as MF. The yield in this conventional teechnique was practically the same as in MW.

Crystalline phase composition of prepared samples was determined by the X-ray diffractometer MiniFlex 600 (Rigaku, Japan) with a Cu-Kα X-ray source ($\lambda = 1.5418$ Å) in the diffraction angle range 5–40° 2θ. The morphology was investigated by the scanning electron microscope NovaNano SEM 450 (FEI Company, The Netherlands). Transmission electron microscopy was employed for obtaining high magnification images by the use of the JEOL JEM 2100 (JEOL, Japan). The photoluminescence (PL) spectra were measured at room temperature by an upgraded Fluorescence spectrometer FLS 920 (Edinburgh Instruments) equipped with Xe lamp (150 W) with monochromatized light as the excitation source. Diffusion reflectance spectra (DRS) were acquired by the UV–Vis spectrometer Avantes AvaSpec using integral sphere with diameter of 50 mm. FT-IR spectra were collected with the aid of FT-IR spectrometer Nicolet 6700 using ATR accessory. The specific surface area was calculated based upon the BET analysis of nitrogen adsorption/desorption isotherms at 77 K recorded by Belsorp-mini II (BEL Japan, Inc.).

Photocatalytic activities of samples were assessed by monitoring degradation rate of Methyl Violet 2B (Sigma Aldrich) solution with the concentration of 3.5 mg/1 L under the UV illumination (focused UV lamp C10 A-HE, wavelength 365 nm). Prior to the experiment, suspension containing 20 mg of investigated powder in 50 mL of dye solution was magnetically stirred in dark for 1 h to reach adsorption equilibrium. The solution was then illuminated by UV lamp while further stirred. The temperature of suspension was maintained at 20 °C. Sample volume of 1 mL was collected into disposable PS cuvette at the beginning of photocatalytic reaction and then at fixed time intervals. Samples were diluted by addition of 2 mL of deionized (DI) water prior to the measurements of UV-VIS absorption (UV–Vis spectrophotometer Cary 300, Varian Inc.).

3. Results and discussion

Crystalline phase composition of synthesized materials was investigated with X-ray (XRD) diffractometry and resulting XRD patterns are shown in Fig. 1. Two characteristic peaks of g-C_3N_4 located above 13° and 27° 2θ yet with small variations in their position allow to identify the material [4]. It can be seen, that all diffractograms are dominated by the peak centred at $2\theta = 27.4°$ which is characteristic for interplanar stacking of aromatic systems and is indexed for graphitic materials as the (002) plane. Without further detailed analysis as the data quality illustrated in diffractograms is moderate, trends can be evaluated. The FWHM of the prominent 002 peak is independent on the synthesis time and has relatively large value about 2.83° 2θ which