General and Inorganic Chemistry

Preparation of sphere-shaped nanoscale carbon nitride polymer

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The carbon nitride polymer of the previously unknown sphere-shaped structure was prepared both by a template-directed solid-state and solution phase syntheses from cyanuric chloride or fluoride and lithium nitride. The obtained polymer powder was characterized by SEM/EDAX, TEM, XRD, TGA, XPS, (^{13}C) MAS NMR, LD/MS, FTIR, UV-visible, and Raman spectroscopy. Modification of the surface area of the template used demonstrated the possibility of producing the carbon nitride spheres with the particle sizes ranging from 20 μm to 50 nm. According to TEM data, the spheres are hollow and the material is shown to be essentially amorphous by powder XRD.

Key words: carbon nitride, polymer synthesis, carbon nanoscale materials, instrumental analysis, materials characterization.

Novel carbon materials, such as heterodiamonds, built from the sp^3-state carbon atoms covalently bonded to a heteroatoms (B, N, Si, or P), are expected to find various applications due to their outstanding hardness, wear resistance, thermal conductivity, and wide bandgap semiconducting properties. According to the early theoretical prediction,[1—3] the carbon nitride with the C_3N_4 stoichiometry and the crystal structure analogous to β-Si_3N_4 should exhibit a bulk modulus higher than that of diamond, which is the hardest known material today. In addition to the β-phase, the existence of other potentially superhard α-, cubic, and pseudocubic crystallographic polymorphs of carbon nitride, C_3N_4, have been suggested on the basis of calculations.[4,5] However, all these phases are predicted to be metastable with respect to the energetically most favorable graphitic carbon nitride, g-C_3H_4, which, due to the sp^2-bonded carbon, is expected to be a fairly soft material.[6] This circumstance, as well as the low thermodynamic stability with respect to the elements (C and N_2), indicated by a positive values of enthalpies of formation,[7] present the most serious obstacles to overcome in the preparation of these phases. Hundreds of documented experimental efforts to produce these materials have typically employed various physical and chemical thin film deposition techniques which led to predominantly amorphous and nitrogen-deficient materials.[8,9] Despite dozens of claims regarding the observation and identification of tiny nano- or micron-size α-, β-, or cubic C_3N_4 crystallites embedded in the amorphous carbon nitride films,[8,10—13] the preparation of larger crystals for precise characterization and mechanical property testing still remains to be accomplished in order both to check the reliability of these claims and verify earlier theoretical predictions.

These goals can be more likely achieved with the help of a recently adopted strategy exploring the high pressure-high temperature synthesis of the C_3N_4 poly-

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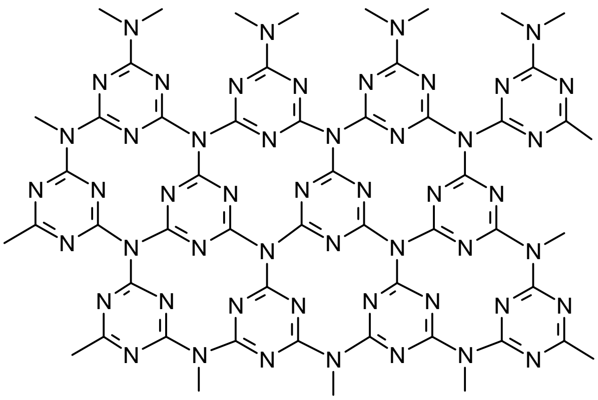
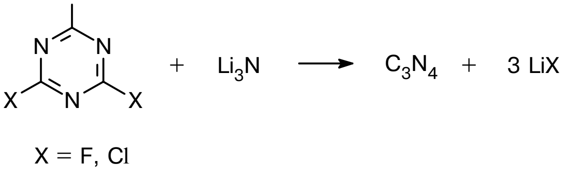


Fig. 1. The 3-fold N-bridged *s*-triazine ring structure of graphite-like C_3N_4.

morphs from suitable precursors[14—17], given well-known successes in application of the high pressure techniques for production of metastable hard materials, *e.g.*, diamond and cubic BN from graphite and hexagonal BN, respectively. The utilization of a similar approach in the case of C_3N_4 materials requires the availability of macroscopic samples of the sp^2-bonded graphitic form of carbon nitride.[4,5,16—21] To solve this problem, we have recently developed an inexpensive solid-state synthesis of the amorphous powder, possessing the correct C_3N_4 stoichiometry and a graphite-like structure (Fig. 1). This amorphous (a-C_3N_4) polymer was prepared in gram quantities in a closed-tight metal reactor[14,15] by a high-temperature polycondensation reaction (Scheme 1) using lithium nitride Li_3N as a nitridation and cross-linking agent and a cyanuric chloride $C_3N_3Cl_3$ or its fluoro analog $C_3N_3F_3$ as an *s*-triazine building block. The accordingly synthesized polymer material is a dark-brown powder which shows featureless morphology with grain particle sizes exceeding 100 μm. The nanoscale-size carbon nitride possessing the previously unknown spherical structure was prepared by us a short time ago[22—24] through modification of the aforementioned reaction (see Scheme 1) by introduction of various porous substrates into the metal reactor or by conducting the whole process in a solution. The results of this most recent work are discussed in the present paper.

Scheme 1



Experimental

Cyanuric chloride (99%, Sigma/Aldrich) was sublimated twice in a vacuum before the use. Cyanuric fluoride (99%, Alfa) and lithium nitride (99.5%, Strem) were used as received. Solid-state syntheses were performed in a stainless steel reactor similar to that described previously.[14,15] In these experiments the cyanuric fluoride or chloride was taken in slight excess relative to lithium nitride to reduce the amount of lithium termination in the final polymer product. The reagents were mixed together in an nitrogen-filled dry box and loaded into the reactor, where various porous substrates were inserted. The substrates included either quartz tubing, microscope slides, quartz wool, carbon fiber or nanosize silica SiO_2 spheres, prepared by colloidal synthesis from tetraethoxysilane according to a known procedure.[25,26] After loading, the reactor was sealed with a leak-tight con-flat cap, taken out of the dry box, and placed into a vertical furnace. The furnace temperature was slowly raised to ~500 °C (which resulted in the heating of the substrate inside the reactor to ~400 °C), held for about 1 h, and then brought back to room temperature. The reactor was then opened, and the substrate removed. At this point the yellow-colored deposit on the substrate used was found due to the presence of nanoscale carbon nitride particles. The substrates were washed with distilled water and the supernatant fluid filtered through a 0.2 μm Cole—Parmer Teflon filter membrane to remove the water-soluble reaction byproduct LiCl (or LiF). The collected yellow polymer product was then dried first on a filter and then in a vacuum oven overnight at ~200 °C. The yield of nanoscale carbon nitride in these experiments was at most 10%.

The solution phase synthesis was carried out in a 250-mL Pyrex flask by adding 5.2 mmoles of lithium nitride and 10.4 mmoles of cyanuric chloride to 150 mL of dry diglyme in a glove box and then refluxing from 8 to 48 h under nitrogen. The color of the solution changed from dark reddish-brown at the very beginning to deep-yellow at the end. After cooling to room temperature, the slowly precipitating fine powder was separated by filtering off diglyme and washing the precipitate on a filter by ethanol and water, followed by drying in a vacuum oven. The final yield of thus prepared carbon nitride polymer can be as high as 95%.

The FTIR spectra of the carbon nitride powders, pressed into a KBr pellet, were collected on a Perkin—Elmer Paragon 1000 FTIR spectrometer with 1 cm^{-1} resolution. UV-Vis spectra were recorded on a GBC UV/VIS 918 spectrophotometer. XPS data were collected with the help of a Physical Electronics PHI 7500 X-ray photoelectron spectrometer using an Al-Kα radiation source (1486.6 eV) with a power setting of 350 W and an analyzer pass energy of 23.5 eV. Graphite powder was used as a reference for calibration of binding energy scale, and a 90% Gaussian and 10% Lorentzian curve fit combination was utilized in the deconvolution procedure of C1s and N1s peaks.

^{13}C MAS NMR spectra of powders packed into a 7-mm rotor were recorded using a Bruker Instruments 200 MHz spectrometer with a 90° pulse width of 4 μs and a relaxation delay of 10 s and referenced to ^{13}C chemical shift of the glycine carbonyl group at δ 176.2. Thermal gravimetric analyses (TGA) were done using a TA Instruments TGA-DTA 2960 analyzer. Scanning electron microscopy (SEM) was carried out at 30 kV beam energy using a JEOL model JSM-6320F field emission microscope equipped with an energy dispersive attenuated X-ray (EDAX) analyzer. Transmission electron microscopy (TEM) photoimages of specimen placed on carbon coated copper grids (size 200 mesh) were obtained with a JEOL JEM-2010 electron microscope operating at an accelerating voltage of 200 kV. X-ray diffraction data were collected on a Rigaku D/MAX-2500H diffractometer with horizontal θ/2θ goniometer using a rotating anode as the Cu-Kα radiation source.

Results and Discussion

The formation of spherical carbon nitride particles was initially observed in the experimental runs in the reactor with the inserted low surface area substrates, such as quartz tubing or microscope slides. However, according to the SEM analysis, only a few spherical particles with average size of 20 μm are produced on these substrates. The dominant product is the amorphous carbon nitride film showing a previously observed featureless morphology.[9,14,15]

The number of spherical particles formed sharply increased by using a quartz wool or carbon fiber as a substrate with a large surface area. The increase in surface area very likely allowed for a greater number of nucleation sites. This resulted in the formation of smaller spheres as the dominant product in the 1 μm to 200 nm size range as observed by SEM (Fig. 2). The smallest sphere size found in these experiments was as low as 50 nm. The TEM studies confirmed the spherical structure of this material and revealed a hollow center of the particles with their inner space size varying along with the exterior dimension (Fig. 3).

The FTIR spectrum of the nano-size spheres provides more information about their chemical structure. The bands observed in this spectrum (Fig. 4) resemble those which characterize the bulk-size C_3N_4 powder with the N-bridged triazine structure (Fig. 1) synthesized at lower temperatures (300 °C) in a Monel reactor.[14,15] The peaks at 807, 1440, 1490, and 1574 cm^{-1} can be assigned to *s*-triazine ring modes, while the peaks in the 1000—1350 cm^{-1} region can be attributed to the C—N stretching modes.[27] The spectrum also shows broad bands of the stretching and deformation modes of the NH and NH_2 groups at 3342 and 1620 cm^{-1} with a possible contribution from OH group vibrations in this region. A very weak band at 2177 cm^{-1} of the cyano group stretch is present in this spectrum as well. These functional groups are known to be introduced by partial destruction of *s*-triazine rings during highly exothermic synthesis process (see Scheme 1) and probably in part by side reaction with water during work-up procedure.[14,15,28]

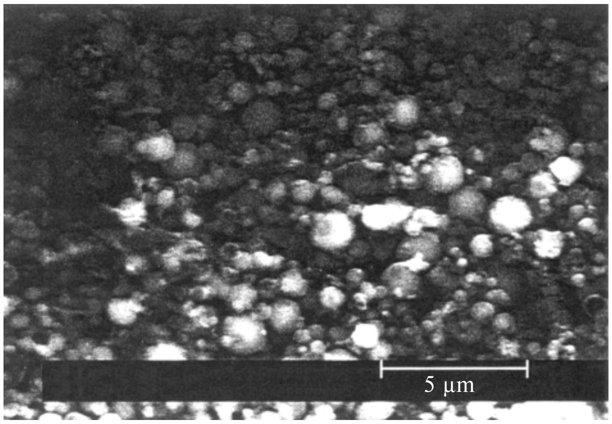


Fig. 2. SEM image of carbon nitride spheres.

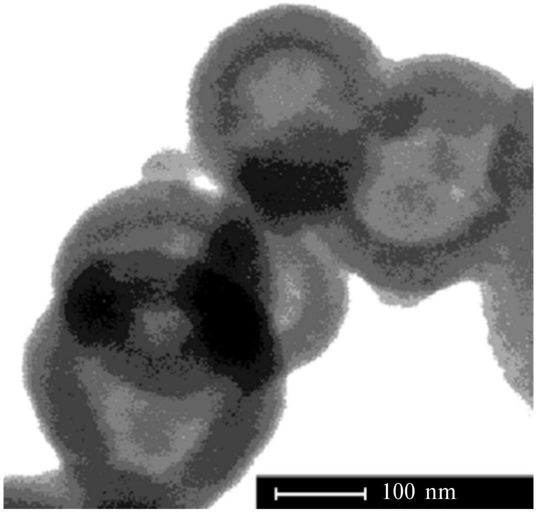


Fig. 3. TEM black and white images of hollow carbon nitride spheres.

The elemental analysis of the nanospheres by EDAX established their nitrogen-rich composition yielding a 31 wt.% carbon and 58% nitrogen in comparison with the 39 wt.% C and 61% N calculated for the C_3N_4 stoichiometry. Also found was a 10 wt.% content of oxygen, which is probably due not only to covalent bonding but also physisorption of O_2 on the polymer material surface. The spherical carbon nitrides are more easily suspendable in alcohol than the bulk-size C_3N_4 powder prepared previously,[14,15] which is a feature of their nanoscopic length scale.

The presence of triazine rings in the nanoscale polymer structure is indicated by observation of a broad band at ~305 nm in the UV spectrum (Fig. 5) of a bright-yellow clear suspension produced by sonication of nano-size carbon nitride spheres in ethanol. This absorption, normally attributed to the π—π* electronic transition in the aromatic 1,3,5-triazine compounds,[28] was observed to shift to 285 nm in the UV spectrum of a micron-size spheres (see Fig. 5). For comparison, a larger blue shift (to 250 nm) of this transition was earlier measured for

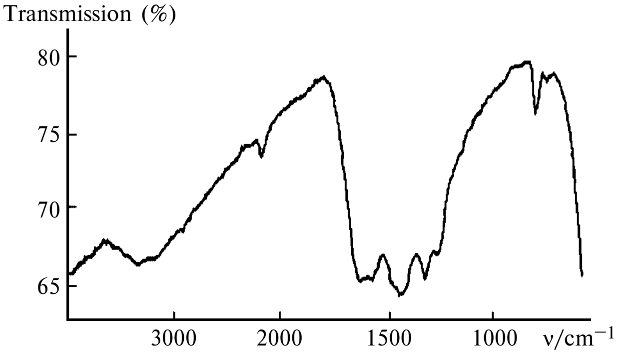


Fig. 4. FTIR spectrum of spherical carbon nitride powder.

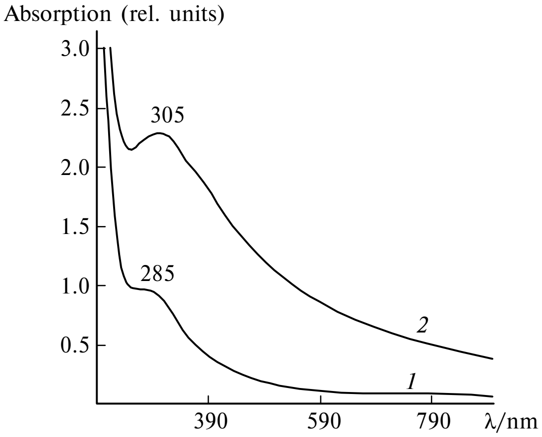


Fig. 5. UV-visible spectra of ethanol solution of carbon nitride spheres: micron-size (*1*) and nanoscale-size (*2*).

the bulk-size C_3N_4 polymer.[15] These observations clearly demonstrate that the location of the UV absorption band in the carbon nitride is dependent on the particle size, which could be important for opto-electronic applications.

The TGA data plot shown on Figure 6 demonstrates that the nanoscale carbon nitride is somewhat less thermally stable than the bulk-size material. Major weight loss in argon is observed at the temperatures above 450 °C for the former, as compared to the 550 °C found earlier for the latter.[15]

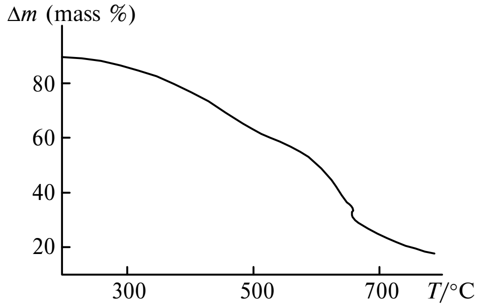


Fig. 6. TGA data plot for spherical carbon nitride in argon.

The laser desorption mass spectrum of the carbon nitride nanospheres (Fig. 7) was produced by ablation of the material with a 337 nm nitrogen laser into smaller fragments, which are then detected by a time-of-flight mass spectrometer. In this spectrum a series of peaks separated by 28 *m*/*z* units indicate the loss of several N_2 molecules, while the peaks differing by 26 *m*/*z* units serve as evidence for the loss of CN fragments. These observed fragmentation routes are consistent with the occurrence of N-bridged triazine rings in the polymer structure. Although we were unable to unambiguously identify the observed fragments, the presence of such large molecular weight C_xN_y species as 550.6, 522.6, 494.6, and 284.3 *m*/*z* implies that these carbon nitrides could find application as novel laser ablated targets in the deposition of the carbon-nitrogen thin films.

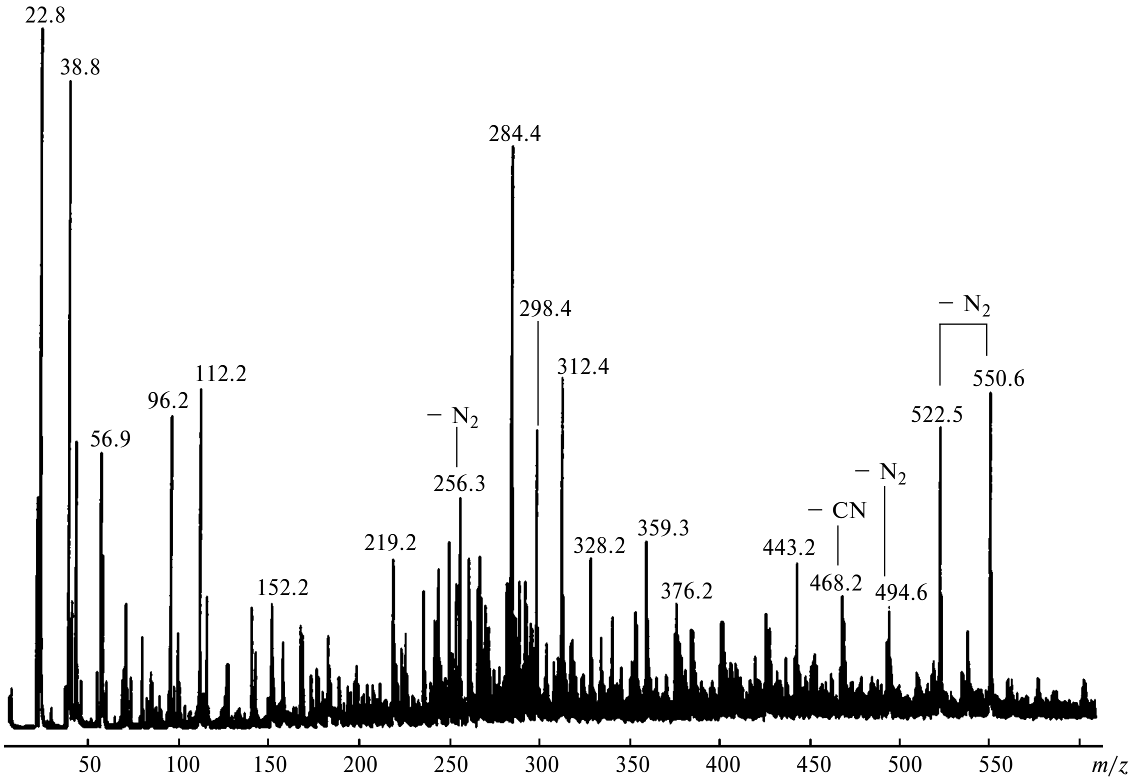


Fig. 7. Laser desorption (337 nm) mass spectrum of spherical carbon nitride polymer.

An important factor in controlling the properties and application of the carbon nitride nanoparticles will be the ability to manage their size and also shape, since some particles were observed to form other shapes besides spheres, *e.g.*, the bean shape. The self-assembly process, which we believe creates the nanospheres, is not perfect by itself, resulting in formation of some defective structures and broad particle size distribution. These undesirable effects were reduced in a template-directed synthesis of the carbon nitride developed in order to aid the formation of the nanospheres. In these experiments the silica spheres of ∼330 nm size prepared by colloidal synthesis[25,26] and fabricated into crystalline arrays[29] were used as a template. Several pieces of the silica template (∼2×1×0.5 mm) were placed in the metal reactor above the inserted carbon fiber. At the end of the reaction each silica nanosphere became coated by carbon nitride layers, producing almost monodisperse spheres with the size of ∼350 nm (Fig. 8, *a*). After the synthesis step the silica arrays were taken out and treated with hydrofluoric acid. This chemical etching procedure led to complete removal of silica, as indicated by FTIR spectra shown in Fig. 9, and remarkable conservation of the spherical shape (Fig. 8, *b*) and near C_3N_4 composition of the carbon nitride verified by SEM/EDAX analysis.

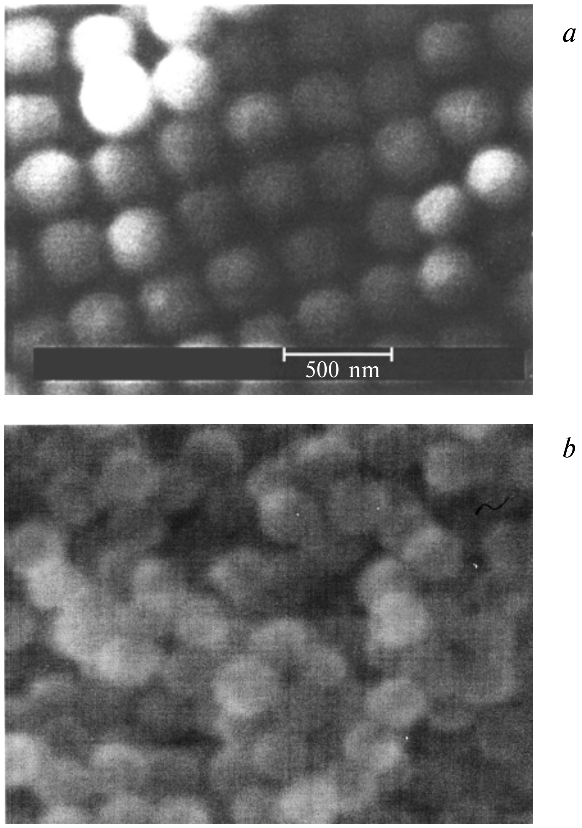


Fig. 8. SEM images taken before (*a*) and after (*b*) treatment with HF acid of monodisperse carbon nitride spheres grown on SiO_2 templates.

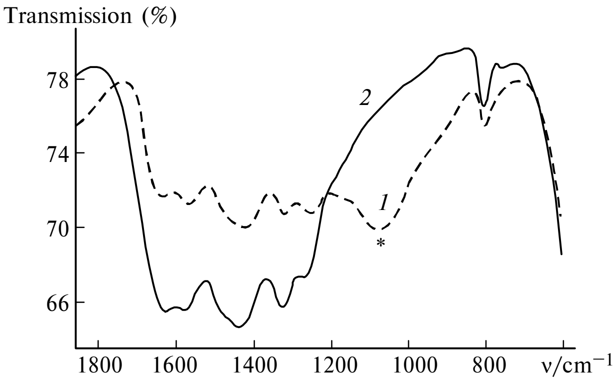


Fig. 9. FTIR spectra of monodisperse carbon nitride spheres grown on SiO_2 templates taken before (*1*) and after treatment with HF acid (*2*), (*) designates SiO_2 absorption.

It is important to note that, prior to our work, a carbon nitride polymer with C_3N_4 stoichiometry and a structure proposed to be built particularly from the 3-fold N-bridged triazine rings (see Fig. 1) has not been observed or theoretically predicted to exist in such an interesting spherical form. The most recent PM3 optimization of the molecular cluster with $C_{24}N_{32}$ composition, which belongs to the C_3N_4 family, yielded the cage structure constructed from the connected eight-membered rings as building blocks[30] resembling arrangement for the β-C_3N_4 phase.[1–3] The fullurene-like microstructure was observed for C_5N thin films in the work.[31] Theoretical MM2 and PM3 calculations have also been reported for the C_{60}-derived $C_{24}N_{36}$ cluster model[32] and for the tubular forms of graphitic carbon nitrides.[30,33,34] All these studies agree in predicting the possibility of curved structures for various carbon nitride phases, which are dictated by pyramidal geometry of bridging nitrogen atoms. Our own MM2 molecular modeling of the carbon nitride oligomer comprising ten triazine rings connected by nine three-coordinated nitrogen atoms yielded not a planar but a shallow bowl structure for the total energy minimum. This structure (Fig. 10), with the outer bridging nitrogen atoms and the end carbon atoms terminated by lithium and F atoms, respectively, helps to explain the growth mechanism of the spherical nanoparticles by a likely formation of curved oligomers as intermediates in the reaction (see Scheme 1). These types of low molecular weight gaseous oligomers, formed at a high temperature, have enough mobility to migrate to the colder (<200 °C) substrate surface and then continue the growth on this reaction site with the growing nanoparticle by self-assembling into a preferred conformation. In the earlier experiments[14,15] the translational and conformational mobility of the intermediate oligomers was probably limited due to their confinement in the solid state, which could explain the formation of a bulk-size particles with a near plane graphitic structure (see Fig. 1) instead of a sphere.

Conducting this reaction in the solution phase was expected to facilitate a free self-assembling of the oligo-

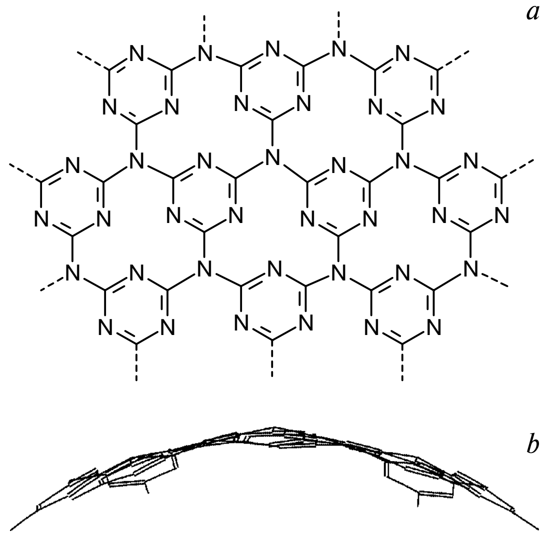


Fig. 10. Curved geometry of the carbon nitride oligomer optimized by MM2 molecular modeling: top view (*a*) and side view (*b*).

mer species. The key point for such a reaction to proceed is the solubilizing of lithium nitride. We selected diglyme as the best solvent for this purpose, based on the recent work.[35] By carrying out the reaction in refluxing diglyme, the sphere-shaped carbon nitride was prepared in a near quantitative yield. Due to the lower reaction temperature in diglyme (b.p. 162 °C), almost no signs of side decomposition of triazine rings, such as the C≡N group features, were observed in the FTIR (Fig. 11) and ^{13}C MAS NMR spectra (Fig. 12) of the nanospheres prepared by the solution-phase synthesis. A strong peak at δ 165.2 with a shoulder at 157.4 ppm in the ^{13}C MAS NMR spectrum (see Fig. 12) is characteristic of the sp^2-hybridized carbons from the *s*-triazine rings.[28,36] The peak of the sp-carbon of the cyano group at δ ~123, observed earlier for the bulk-size C_3N_4 powder prepared by the solid-state method,[14,15] is practically absent in this spectrum. However, the presence of diglyme solvent peaks in the δ 40—72 region is noticeable. The annealing of the sample at 160 °C *in vacuo* over 48 h failed to remove this solvent completely and only helped to reduce its content to as low as 5%, as established by relative integration of the diglyme and triazine peaks. This can be very likely explained by the residual diglyme trapped inside the carbon nitride spheres.

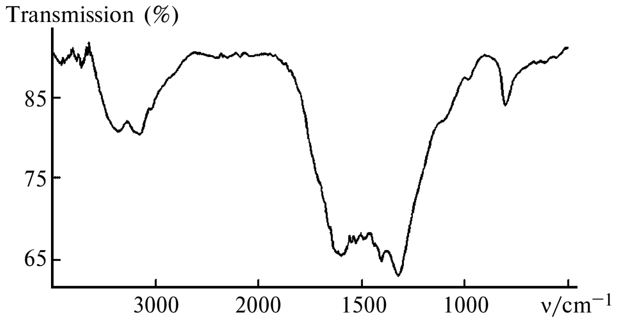


Fig. 11. FTIR spectrum of spherical carbon nitride from solution phase synthesis.

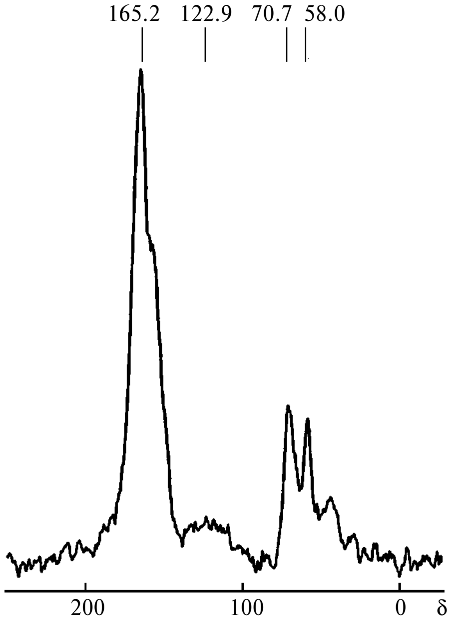


Fig. 12. ^{13}C MAS NMR spectrum of spherical carbon nitride polymer powder.

The presence of diglyme in the polymer structure likely accounts for the increase of the C to N wt.% ratio to 0.8* in comparison with that theoretically expected for C_3N_4 (0.64). This is also witnessed by the XPS data. The survey scan spectra indicate the presence of only C and N in addition to a smaller amount of O. The C1s peak (Fig. 13, *a*) deconvolutes into five components at binding energies of 284.8, 285.7, 287.0, 289.0 (major component), and 290.1 eV, which can be assigned to the carbon atoms in the C—C, C—O (both mainly from the diglyme), C≡N (originating from partial cleavage of triazine rings under X-ray irradiation), and *s*-triazine C=N bonds, respectively.[37] The very weak component at 290.1 eV, noted to be reduced by Ar ion beam sputtering, is probably related to the adsorbed contaminants.[38] The deconvoluted N1s peak (Fig. 13, *b*) shows a major component at 399.5 eV due to the sp^2 nitrogen in the *s*-triazine rings from the curved graphite-like structure envisioned for the carbon nitride spheres by the molecular modeling (see Fig. 10). The smaller component at ~401 eV can be attributed to the pyramidalized sp^3 nitrogen atoms from the 3-fold N-bridging units. However, the observed in Fig. 13, *b* ratio of integrated peak area for this minor component relatively to that of major component is higher than theoretically expected (~1 : 2 *vs.* 1 : 3, respectively). This strongly suggest some additional contribution into a minor component from sp^3 nitrogens of —NH— bridges, which, according to IR

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* Elemental analysis was performed at the Galbraith Laboratories, Inc.

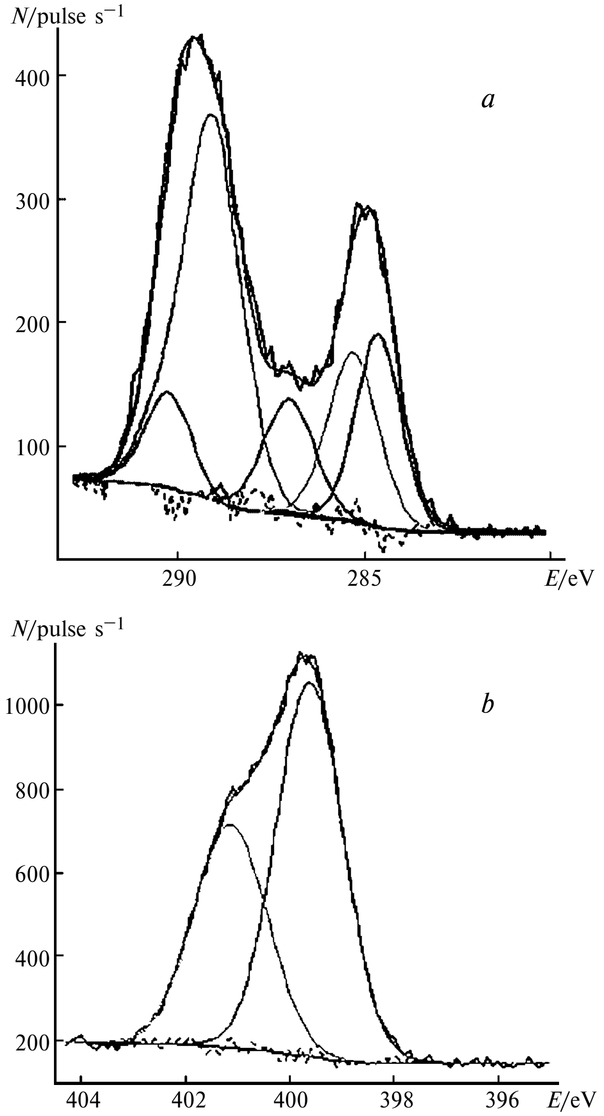

Fig. 13. Deconvolution of the C1s (*a*) and N1s (*b*) peaks in the XPS spectrum of spherical carbon nitride.

spectrum (see Fig. 11), are also present, as well as an input from sp nitrogen atoms of the C≡N terminal groups formed under X-ray beam during the XPS analysis.

In the powder XRD spectrum the material prepared by diglyme synthesis shows a very weak broad feature in the 2θ region from 20° to 30°. These data along with the observed diffuse ring pattern in TEM microdiffraction indicate the essentially amorphous structure of this material.

In should be noted in conclusion that the preparation of a novel form of carbon nitride has been achieved in this work with the use of commercially available low cost reagents, which enable large-scale production. Besides use as a precursor for the high pressure—high temperature synthesis of crystalline C_3N_4 phases,[39] the spherical carbon nitride has a potential for applications in coatings, lubricants, catalyst supports, gas storage, as well as for drug delivery, in view of the possibility of chemical functionalization.

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References

1. M. L. Cohen, *Phys. Rev., B,* 1985, **32**, 7988.
2. A. Y. Liu and M. L. Cohen, *Science*, 1989, **245**, 841.
3. A. Y. Liu and M. L. Cohen, *Phys. Rev., B*, 1990, **41**, 10727.
4. A. Y. Liu and R. M. Wentzcovitch, *Phys. Rev., B*, 1994, **50**, 10362.
5. D. M. Teter and R. J. Hemley, *Science*, 1996, **271**, 53.
6. P. N. Wang, Z. Guo, X. T. Ying, J. H. Chen, X. M. Xu, and F. M. Li, *Phys. Rev., B*, 1999, **59**, 13347.
7. D. C. Nesting and J. V. Badding, *Chem. Mater.*, 1996, **8**, 1535.
8. E.-G. Wang, *Adv. Mater.*, 1999, **11**, 1129 and references cited therein.
9. V. N. Khabashesku, J. L. Margrave, K. Waters, and J. A. Schultz, *Thin Solid Films*, 2001, **381**, 62 and references cited therein.
10. C. M. Niu, Y. Z. Lu, and C. M. Lieber, *Science*, 1993, **261**, 334.
11. D. M. Bhusari, C. K. Chen, K. H. Chen, T. J. Chen, L. C. Chen, and M. C. Li, *J. Mater. Res.*, 1997, **12**, 322.
12. J. Hu, P. Yang, and C. M. Lieber, *Phys. Rev., B*, 1998, **57**, 3185.
13. Z. Zhang, H. Guo, G. Zhong, F. Yu, Q. Xiong, and X. Fan, *Thin Solid Films*, 1999, **346**, 96.
14. V. N. Khabashesku, J. L. Zimmerman, and J. L. Margrave, Invention disclosure. Filed at Rice University in February 1999. Patent conversion filed with the US Patent and Trademark Office on July 27, 2000.
15. V. N. Khabashesku, J. L. Zimmerman, and J. L. Margrave, *Chem. Mater.*, 2000, **12**, 3264.
16. I. Alves, G. Demazeau, B. Tanguy, and F. Weill, *Solid State Commun.,* 1999, **109**, 697.
17. H. Montigaud, B. Tanguy, G. Demazeau, I. Alves, and S. Courjault, *J. Mater. Sci.,* 2000, **35**, 2547.
18. J. Kouvetakis, A. Bandari, M. Todd, and B. Wilkens, *Chem. Mater.*, 1994, **6**, 811.
19. J. E. Lowther, *Phys. Rev., B*, 1999, **59**, 11683.
20. M. Mattesini, S. F. Matar, A. Snis, J. Etourneau, and A. Mavromaras, *J. Mater. Chem.,* 1999, **9**, 3151.
21. M. Mattesini, S. F. Matar, and J. Etourneau, *J. Mater. Chem.*, 2000, **10**, 709.
22. J. L. Zimmerman, Ph. D. Thesis, Rice University, April 2000, Houston, TX.
23. R. Williams, J. Zimmerman, V. Khabashesku, and J. Margrave, *Rice Quantum Institute Fourteenth Annual Summer Research Colloquium, August 11, 2000, Abstrs.,* Rice University, Houston, TX, USA, 2000, 22.

24. J. L. Zimmerman, V. N. Khabashesku, and J. L. Margrave, *220th Nat. ACS Meeting. Div. of Industr. Engineering. Chem. Topic — Advanced Materials and Nanotechnology: Nanostructured Materials, I, August 20—24, 2000, Abstrs.*, Washington, D.C., 2000, 190.
25. W. Stober, A. Fink, and E. Bohn, *J. Colloid Interface Sci.,* 1968, **26**, 62.
26. G. H. Bogush, M. A. Tracy, and C. F. Zukoski, IV, *J. Non-Cryst. Solids*, 1988, **104**, 95.
27. D. Lin-Vien, N. B. Colthup, W. G. Fatelley, and J. G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press Inc., San Diego, CA, 1991, p. 299.
28. J. M. E. Quirke, *1,3,5-Triazines*, in *Comprehensive Heterocyclic Chemistry*, Ed. A. R. Katritzky, Pergamon Press, Oxford—New York—Toronto—Sydney—Paris—Frankfurt, 1984, **3**, 457.
29. P. Jiang, J. F. Bertone, K. S. Hwang, and V. L. Colvin, *Chem. Mater.,* 1999, **11**, 2132.
30. M. C. dos Santos and F. Alvarez, *Phys. Rev., B,* 1998, **58**, 13918.
31. H. Sjöström, S. Stafström, M. Boman, and J.-E. Sundgren, *Phys. Rev. Lett.,* 1995, **75**, 1336.
32. Y. Muramatsu, T. Hayashi, and R. C. C. Perera, *J. Electron Spectrosc. Related Phenom.*, 1999, **104**, 155.
33. Y. Miyamoto, M. L. Cohen, and S. G. Louie, *Solid State Commun.,* 1997, **102**, 605.
34. S. Ren, B. C. Satishkumar, A. Govindaraj, K. R. Harikumar, G. Raina, J.-P. Zhang, A. K. Cheetham, and C. N. R. Rao, *Chem. Phys. Lett.,* 1998, **287**, 671.
35. J. E. Bender, IV, W. Chin, and M. M. Banaszak Hall, *Chem. Mater.,* 1999, **11**, 154.
36. F. W. Wehrli and T. Wirthlin, *Interpretation of Carbon-13 NMR Spectra*, Heyden, London—New York—Rheine, 1976.
37. G. Beamson and D. Briggs, *High Resolution XPS of Organic Polymers,* Wiley, New York, 1992.
38. T. Komatsu and T. Nakamura, *J. Mater. Chem.,* 2001, **11**, 474.
39. V. N. Khabashesku, B. Brinson, J. L. Margrave, V. A. Davydov, L. S. Kashevarova, A. V. Rakhmanina, and E. N. Yakovlev, *J. Phys. Chem., B*, 2002, in press.

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