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Synthesis of Spherical Carbon Nitride Nanostructures

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ABSTRACT

Carbon nitride spheres, with diameters ranging from 20 microns to as few as 30 nanometers were prepared by template-directed solid-state or solution reaction of cyanuric chloride or fluoride with lithium nitride. The electron microscopy data on the hollow spheres suggest their multiwalled nanostructure, built by disorderly stacked C_3N_4 curved layers assembled from triazine rings and nitrogen bridges of pyramidal structure. The closed spherical shape of this form of carbon nitride suggests its use in lubricants, catalyst supports, gas storage, and drug delivery.

Carbon nitride (C_3N_4) became an extremely desirable material to produce in view of theoretical predictions[1−5] that the hexagonal (α- and β-), cubic (c-) and pseudo-cubic C_3N_4 polymorphs may possibly be harder than diamond. Many research teams have claimed the observation of tiny micron-size α-, β-, and c−C_3N_4 crystallites in thin films;[6−12] nevertheless, the production of a larger crystals for precise characterization has not been yet accomplished. Graphitic forms of carbon nitride, g−C_3N_4, have attracted theoretical[4,5,13−15] and experimental[16−20] attention as well for their potential application as organic semiconductors and precursors for superhard phases.

Graphite-like carbon materials are known for their ability to adopt spheroid microstructures, e. g., in fullerenes and their relatives, single-wall and multiwall carbon nanotubes. Substitution of carbon by nitrogen in the planar graphitic structure was predicted to lead to closed forms as well, occurring at N/C atomic ratio greater than 0.2.[21] The possibility of curved structures for carbon nitride phases should be dictated by pyramidal geometry of bridging nitrogen atoms. Indeed, the observations of fullerene-like microstructures[22] and carbon nitride nanotubes[6] of the C_5N stoichiometry as well as C_3N_2 nanocage structures in the material with C_3N_4 bulk composition[23] have been reported. For the nitrogen-rich compositions, such as C_1N_1 and $C_{24}N_{36}$, theoretical calculations also predicted graphitic tubular forms[21,24,25] and a C_{60}-derived cage structure,[26] respectively. The PM3 optimization of the molecular cluster with $C_{24}N_{32}$ composition,[21] which belongs to the C_3N_4 family, yielded the closed cage structure constructed from the connected eight-membered rings as building blocks resembling arrangement for the β-C_3N_4 phase.[1−3] However, a spherical carbon nitride with C_3N_4 stoichiometry has not been observed experimentally until recently.[27−30] Here we report a synthesis of this new form of carbon nitride, which has a closed spherical structure built from the N-bridged six-membered triazine rings.

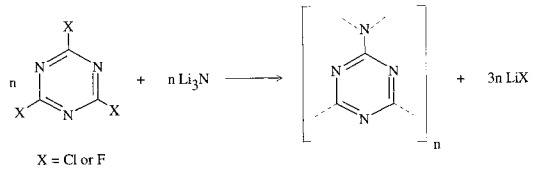

Figure 1. General reaction scheme for carbon nitride synthesis. Dashed lines indicate sites for N-bridged polycondensation.

The synthesis of carbon nitride with a high nitrogen content is difficult due to the greater thermodynamic stability of carbon and separate nitrogen molecules.[31] This is likely the reason for the failure of various physical and chemical deposition methods to produce materials with the bulk C_3N_4 composition. The application of chemical synthetic methods, using milder conditions, has proven to be more successful. Recently, we have developed a solid-state synthesis of the amorphous powder, possessing the correct C_3N_4 stoichiometry and a graphite-like structure built from N-bridged s-triazine rings.[19] This material was prepared in gram quantities by a high-temperature reaction using cyanuric chloride or fluoride as an s-triazine building block and lithium nitride Li_3N as a nitrogen-bridging agent (Figure 1). The synthesized powder demonstrated featureless morphology with grain particle sizes exceeding 100 micrometers.

The carbon nitride possessing the previously unknown[27−30] spherical structure was prepared in present work through

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modification of this reaction (Figure 1) by introduction of porous substrates into a steel reactor, described previously,[19,27,28] or by conducting the process in a solution. The substrates included quartz tubing, microscope slides, quartz wool, carbon fiber or nanosize silica spheres, prepared by colloidal synthesis and arranged into crystalline arrays according to described procedure.[32] The reagents, cyanuric fluoride or chloride taken in slight excess to lithium nitride, were mixed in a drybox and loaded into a reactor, where the substrate was inserted. The reactor was sealed, taken out of the drybox and placed into a vertical furnace. The temperature was slowly raised to about 500 °C (which resulted in heating of the substrate to about 400 °C), held for about 1 h, and then brought back to ambient. The reactor was opened and the substrate removed. The deposit on the substrate was washed with distilled water and the supernatant fluid filtered through a 0.2 μm (Cole-Parmer) Teflon membrane to remove reaction byproduct LiCl (or LiF). The yield of the yellow powder, collected from the filter after drying in a vacuum oven at about 200 °C, did not exceed 10%. The solution phase synthesis was carried out in a Pyrex flask by refluxing 5.2 mmol of lithium nitride and 10.4 mmol of cyanuric chloride in 150 mL of dry diglyme during 8 to 48 h under nitrogen. The slowly precipitating yellow powder was filtered of diglyme, washed with ethanol and water, and also dried in a vacuum oven, producing the final yield as high as 95% (calculated for C_3N_4). The synthesized powders were investigated using a transmission electron microscope (TEM; JEOL JEM-2010) with EELS attachment and a scanning electron microscope (SEM; JEOL JSM-6320F) equipped with an energy dispersive attenuated X-ray (EDAX) analyzer, Fourier transform infrared (FTIR; Perkin-Elmer Paragon 1000), solid-state (^{13}C) MAS NMR (Bruker 200 MHz), and powder X-ray diffractometer (XRD; Rigaku D/MAX-2500H) to obtain information on bulk and microstructure and composition.

First experiments, done with low surface area substrates (quartz tubing or microscope slides), produced only a few spherical particles with average size of 20 microns, observed by SEM. The dominant product is the amorphous carbon nitride film showing a previously observed featureless structure.[19] The number of spherical particles was sharply increased by using substrates with a large surface area (quartz wool or carbon fiber), providing a greater number of nucleation sites. This also resulted in formation of smaller size spheres ranging from 1 micron to as low as 30 nm, contrary to 300 nm C_3N_2 nanospheres and nanorods observed under another conditions.[23] The TEM studies revealed a hollow center in the spherical particles (Figure 2). EELS analysis done on the 30 nm size hollow particles (Figure 2b) produced a spectrum, shown on Figure 3. In this spectrum a similar K-edge features of the sp^2-bonded carbon and nitrogen atoms with the sharp peaks at about 284 and 399 eV, respectively, most likely characterize the s-triazine based graphitic carbon nitride network.[18] In the electron microdiffraction these hollow spheres exhibit diffuse ring patterns, indicating a highly disordered wall microstructure, which is possibly multilayered. This agrees with the XRD

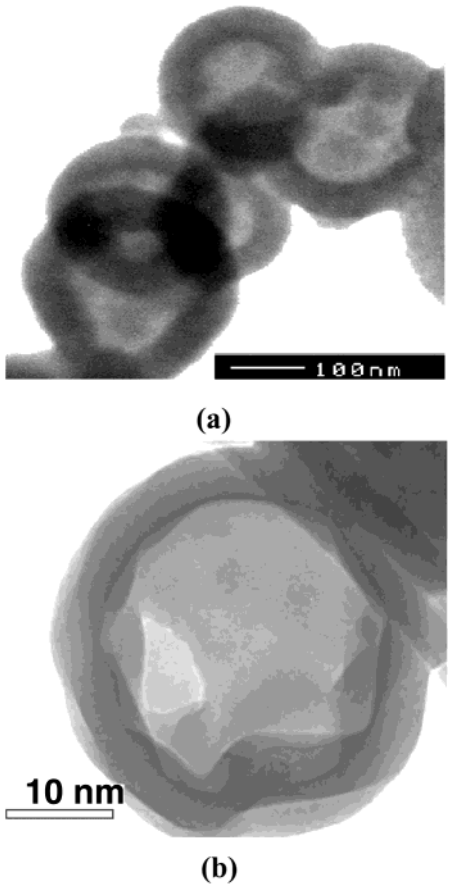

Figure 2. TEM images of hollow carbon nitride spheres. (**a**) 200 nm size (**b**) 30 nm size.

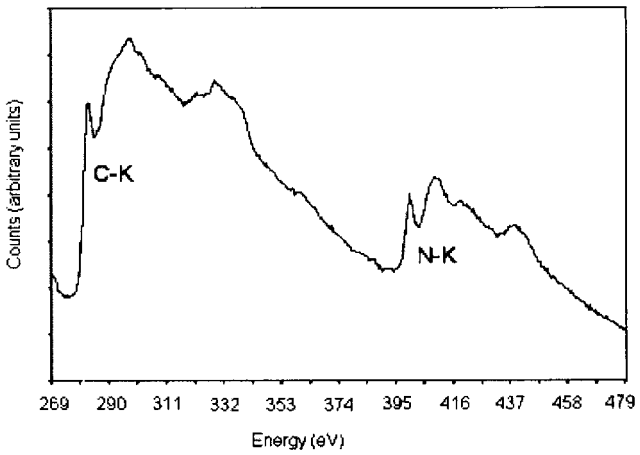

Figure 3. EELS spectrum taken on the wall of carbon nitride sphere shown on Figure 2b.

observation of a single broad peak at $2\theta = 25.8°$ corresponding to interlayer *d* spacing of 3.415 Å, very close to the intershell spacing (3.42 Å) in the multiwall carbon nanotubes[33] built from rolled graphene sheets. The observed larger *d* spacing in spheric carbon nitride than that predicted for g$-C_3N_4$ (3.29 Å)[13] seems reasonable in view of the increased interlayer spacing in the muti-wall carbon nanotubes with respect to interplanar distance (3.34 Å) in graphite.

The FTIR spectrum (Figure 4a) of nanosize spheres resembles that of bulk-size C_3N_4 powder possessing the

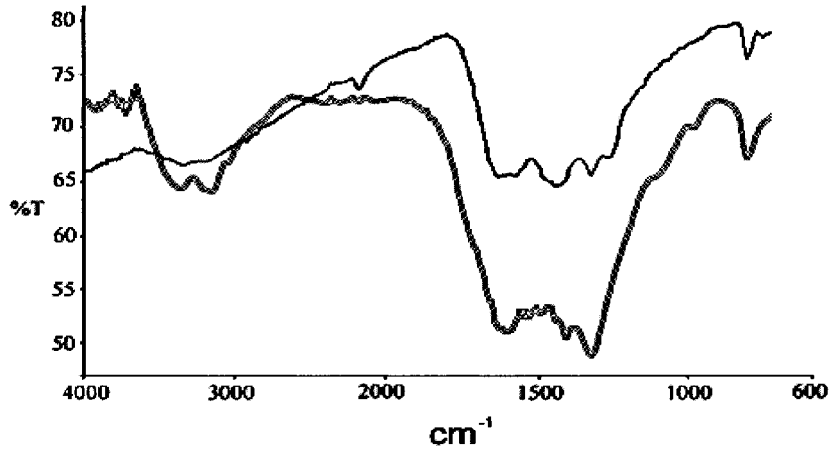

Figure 4. FTIR spectra of spherical carbon nitrides pressed in the KBr pellet. Top thin line shows the trace for material from solid-state synthesis, while the bottom broad line shows the trace for material prepared by solution synthesis in diglyme.

N-bridged s-triazine structure.[19] The peaks at 807, 1440, 1490 and 1574 cm^{-1} belong to s-triazine ring modes, while the peaks in the 1000−1350 cm^{-1} region to the C−N stretchings. Also, broad bands of stretching and deformation modes of the NH and NH_2 (and possibly OH) groups at 3342 and 1620 cm^{-1} and a weak band at 2177 cm^{-1} of the C≡N stretch are present. These functional groups arise from partial destruction of s-triazine rings during the highly exothermic synthesis process (Figure 1) and, in part, side reaction with water during the workup procedure.[19,34] This is reflected by the EDAX data on bulk composition of the nanospheres yielding a 31 wt % C, 58% N and 10% O, in comparison with the 39 wt % C and 61% N calculated for the C_3N_4 stoichiometry. The presence of s-triazine rings in the structure is also indicated by absorption at 305 nm due to the $\pi-\pi^*$ electronic transition[34] observed in the UV spectrum of a bright-yellow clear suspension of nanosize spheres in ethanol. This absorption blue-shifts to 285 nm for micron-size spheres and further (to 250 nm) in case of the larger bulk-size C_3N_4 material.[19] Thus, the UV absorption in the carbon nitride is dependent on particle size, which could be important for optoelectronic applications.

By carrying out the reaction (Figure 1) at lower temperature in diglyme (bp 162 °C) the carbon nitride spheres (Figure 5) have been prepared in a near quantitative yield and without a side decompositon of s-triazine rings, demonstrated by absence of the C≡N group features in the FTIR (Figure 4b) and (^{13}C) MAS NMR spectra. However, in the latter spectrum besides peaks at 165.2 and 157.4 ppm of carbons from the s-triazine rings[19,34] the peaks at 40−72 ppm from diglyme solvent (estimated at 5% content) were observed even after heating the sample in a vacuum. This residual diglyme is probably trapped in some of the carbon nitride spheres; therefore, their bulk composition ($C_{0.34}H_{0.03}N_{0.42}O_{0.16}Cl_{0.06}$, Galbraith Laboratories, Inc.) shows an elevated C/N weight % ratio (0.8) in comparison with the theoretically expected for C_3N_4 (0.64) and also an increased content of hydrogen and oxygen with respect to the solid-state synthesis.

The observation of the distinctly new spherical form of carbon nitride formed both in the solid and liquid-phase reactions suggests that it is a fundamental structural feature. To explain the growth mechanism of spherical nanoparticles, we have carried out a molecular modeling (MM2) of the structure of oligomer comprising 10 triazine rings connected by nine three-coordinated nitrogens (Figure 6a). The optimized geometry of this oligomer was found to be not planar but shallow bowl-shaped (Figure 6b). Such oligomers are likely formed as a mobile intermediates in the reaction (Figure 1) and grow into a spherical conformation by self-assembling. In the solid state the limited conformational mobility of the intermediates dictates formation of a bulk-size particles with a near plane graphitic structure.

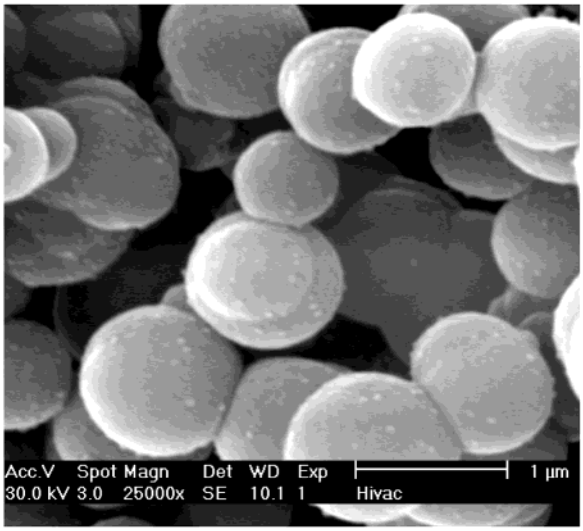

Figure 5. SEM image of carbon nitride spheres prepared in diglyme after coating by gold sputtering.

An important factor in controlling the properties and application of the carbon nitride nanoparticles will be the ability to manage their size and shape. This has been successfully demonstrated in our syntheses using silica spheres (330 nm-size) as templates. At the end of the reaction each silica nanosphere become coated by carbon nitride layers, producing almost monodisperse spheres with the size of about 350 nm. The chemical etching with hydrofluoric acid led to complete removal of silica and remarkable

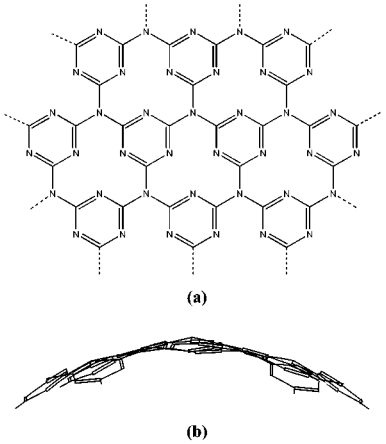

Figure 6. Proposed carbon nitride oligomer structure on basis of MM2 molecular modeling. (**a**) top view (**b**) side view. Dashed lines indicate sites for polymer growth at bridging nitrogens and end carbons terminated by Li and F atoms, respectively.

conservation of the spherical shape and near C_3N_4 composition of the carbon nitride.

In conclusion, it is important to note that preparation of a spherical form of carbon nitride has been achieved with commercially available low cost reagents, which enable large-scale production. Besides use as a precursor for the high pressure-high-temperature synthesis of superhard phases, this nanoscale carbon nitride has a potential for applications arising from its spherical shape and possibility of chemical functionalization and improved processing.

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