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Solid State synthesis and Characterization of Carbo-Nitride Materials

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13. ABSTRACT (Maximum 200 words)

The preparation of stoichiometric sp^2-bonded amorphous carbon nitride a-C_3N_4 in gram quantities was successfully achieved by performing a solid-state reaction of cyanuric halides $C_3N_3X_3$ (X=Cl, F) with lithium nitride L_3N at temperatures 300-380 °C. Addition of boron precursors, e. g., $NaBF_4$, resulted in preparation of a nitrogen-rich B-C-N powder of approximately $B_3C_3N_7$ composition and showing thermal stability up to temperatures of 1000 °C. The densification of micronized powders by cold isothermal pressing has produced disk-shaped ceramics of C_3N_4 and B-C-N materials, being lighter than graphite and boron nitride h-BN, respectively. Further modification of the reaction by introduction of porous substrates and templates has led to preparation of a previously unknown material - sphere-shaped nanoscale-size carbon nitride built by stacking of curved C_3N_4 layers. Preliminary high pressure/high temperature experiments with the C_3N_4 powder as precursor have demonstrated that the structure of carbon nitride changes under pressures of 8 to 12 Gpa from amorphous to a more ordered graphite-like one, retaining the C_3N_4 stoichiometry at temperatures up to 500 °C and losing nitrogen at higher temperatures. The overall amorphous morphology of the carbon nitride has so far precluded the generation of a secondary electron emission by this material during the tests performed. Continuing attempts to prepare crystalline carbo-nitride phases both by the high pressure treatment of amorphous powder precursors and by an appropriate synthetic routes designed are in progress in our laboratory.

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(4) STATEMENT OF THE PROBLEM STUDIED

During the reporting period the initially proposed idea of developing new efficient method for preparation of multielement nitride, carbonitride, and oxynitride thin films and materials has been further explored. Based on our recent success in solid-state synthesis of *stoichiometric* sp^2-bonded carbon nitride, which has made this material available in gram quantities[1,2], we have carried out a series of high pressure experiments in pursuit of large crystals of superhard β-C_3N_4[3-5] and other predicted polymorphs[6-9] while using amorphous *a*-C_3N_4 powder as a precursor. According to SEM (Figure 1), EDAX, micro-Raman and powder X-ray studies, under pressures of 8 to 12 GPa the structure of carbon nitride starts to change from an amorphous one to a more ordered layered graphite-like structure (with interplane d-spacing of about 3.0-3.1 Å), retaining the C_3N_4 stoichiometry at temperatures of up to 400°C and losing nitrogen at higher temperatures (up to 1200°C, as studied) to convert into a pure carbon phase of graphite (d-spacing of 3.34 Å). These preliminary experiments allowed us to determine the temperature range where the structure transformation of carbon nitride starts to occur in the right direction. The experiments under higher pressures (above 12 GPa) will be continued using *a*-C_3N_4 powder precursor and liquid nitrogen and ammonia as a matrix. Besides the C_3N_4 polymer, several molecular C-N precursors will also be studied in these experiments. This work is being done in collaboration with Professor Dr. E. N. Yakovlev and his coworkers at the High Pressure Physics Institute of the Russian Academy of Sciences, Troitsk, Moscow region.

We were also able to perform densification of micronized C_3N_4 powders by cold isothermal pressing (CIP) at 55000 PSI done in Professor K. Salama laboratory in the Department of Mechanical Engineering at the University of Houston. The disk-shaped ceramics formed had the densities of about 1.34-1.38 g/cm^3, being much lighter than graphite (d=2.25 g/cm^3). The linear electric resistivities of these ceramics, measured at about 0.67 Megohm·cm, lie close to those of blue diamond semiconductors. However, because of overall amorphous morphology, the undoped and doped (by Li and B) carbon nitride ceramics did not generate a secondary electron emission during testing for possible application as ion detectors in the time-of-flight mass spectrometers by carrying out measurements at Ionwerks, small business company of Houston (Dr. J. A. Schultz, President). Therefore, further work will be amed at preparation of crystalline phases of carbon nitride.

Modification of solid-state reaction by addition of boron precursor into a reacting mixture of cyanuric chloride $C_3N_3Cl_3$ and lithium nitride Li_3N, used for synthesis of the C_3N_4 powders, has resulted in preparation of nitrogen-rich B-C-N amorphous material of approximately $B_3C_3N_7$ stoichiometry. Insertion of a Ni-foil into this reacting mixture facilitated growth of a B-C-N microfiber phase on the reactor insert surface, as proven by SEM-EDAX technique (Figure 2). Both the C_3N_4 and B-C-N materials are chemically resistant to acids and oxygen. Moreover, introduction of boron into carbon nitride structure causes a dramatic increase in thermal stability of B-C-N material vs. a-C_3N_4, as demonstrated by TGA data plots (Figure 3). The B-C-N disk specimens prepared by CIP procedure are electrically conductive and lighter (d=1.83-1.86 g/cm^3) than the h-BN material (2.28 g/cm^3). Besides the testing for potential application as solid lubricants, ceramic disks of B-C-N and a-C_3N_4 are currently studied for use as targets for laser

ablation and sputtering by nitrogen ion or atomic beam in the deposition processes of potentially ultrahard C-N and B-C-N films. It seems worthwhile to employ in these experiments a combination of the neutralized nitrogen beam assissted method for C-N film deposition at cryogenic temperatures, earlier developed by us[10-13], with the method for preparation and fabrication of C-N and B-C-N ceramic targets, demonstrated in the present work.

Further modification of reaction between cyanuric chloride $C_3N_3Cl_3$ or its fluoro analogue, $C_3N_3F_3$, and lithium nitride Li_3N, by introduction of various porous substrates into the reactor, e. g., quartz tubing, quartz microscope slide, quartz wool, carbon fiber, or porous nanoscale-sized silica as a template has led to a formation of sphere-shaped *nanoscale carbon nitride* powders. It was found that the particle size can be controlled by the surface area of the substrate or template used, to yield carbon nitride nanosize spheres ranging from 40 microns to as small as 50 nm. According to X-ray, SEM, EDAX and TEM (Figure 4), the spheres are hollow and multi-wall built by stacking of curved C_3N_4 layers with the d-spacing of about 3.0 A. This newly discovered spheric structure of carbon nitride agrees with our molecular modeling studies.[14] The opto-electric and mechanical properties of this new material may be unique, therefore, they need to be extensively studied, e.g., for application as a matrix materials in analyses of aminoacids and DNA by MALDI - TOF mass spectrometry, for fabrication of electronic micro- and nanodevices as in situ doped semiconductors, and for use as a solid lubricant.

(5) SUMMARY OF THE MOST IMPORTANT RESULTS

The powder synthesis of amorphous carbon nitride with the stoichiometry very close to C_3N_4 in gram quantities has been achieved in the present work. The demonstrated approach,

which is based on fast solid state reactions, is particularly attractive since: (i) it uses the relatively cheap reagents and does not require synthesis of single-source precursors, as in the previously reported preparation of carbo-nitride[15-17]; (ii) it produces powders with a higher nitrogen content than, for example, the carbon nitride powders of approximately C_4N_5 stoichiometry described in a German patent[17], (iii) the reaction routes, leading to production of covalently bonded not only binary, but also ternary and quaternary carbo-nitride materials with controlled stoichiometry, morphology, mechanical and electric properties can probably be designed. The flexibility of this approach was verified by successful synthesis of amorphous B-C-N powders of approximate $B_3C_3N_7$ stoichiometry. Our work is being currently extended to preparation of other carbo-nitride materials and testing of their mechanic and electric properties.

(6) LIST OF PUBLICATION

During the reporting period five manuscripts, citing financial support from the US Army Research Office, have been submitted for publication. The manuscript titles are listed below:

[1] Matrix Isolation Infrared and Density Functional Theoretical Studies of Cryogenic Reactions of Silicon Atoms with Dimethyl Ether and Methanol. New Route to Generation and Stabilization of Transient Silanones. V. N. Khabashesku*, K. N. Kudin, J. L. Margrave, L. Fredin, *J. Organometal. Chem.*, **2000**, 595, p. 248-260.

[2] Cryogenic deposition of carbon nitride thin films using a neutralized atomic nitrogen beam. V. N. Khabashesku* , J. L. Margrave, K. Waters, J. A. Schultz. *Thin Solid Films*, submitted on March 29, 2000.

[3] Powder synthesis and characterization of amorphous carbon nitride, a-C_3N_4. V. N. Khabashesku,* J. L. Margrave, J. L. Zimmerman, *Chem. Mater.* submitted on April 20, 2000.

[4] Density Functional Theoretical Studies of [2+2] Cycloaddition of Transient Silene and Germene to Formaldehyde, Thioformaldehyde, and Ethylene. V. N. Khabashesku*, K. N. Kudin, J. L. Margrave, *Rus. Chem. Bull.* submitted on June 14, 2000.

[5] Synthesis of Nanoscale Carbon Nitride. J. L. Zimmerman, V. N. Khabashesku, J. L. Margrave, Submitted for oral presentation at the 220th National ACS Meeting. Division of Industrial and Engineering Chemistry. Topic Selection - Advanced Materials and Nanotechnology: Nanostructured Materials I. August 20-24, 2000, Washington, D.C.

(7) PARTICIPAITING SCIENTIFIC PERSONNEL

Professor Dr. Valery N. Khabashesku, who is a lead scientist on this project, has been supported by the current US Army grant at a Senior Research Scientist level at Rice. Besides Professor V. N. Khabashesku, two Graduate Students, Konstantin N. Kudin and John L. Zimmerman, were collaborating on the project. This project was mentored by Dr. J. L. Margrave, E. D. Butcher Professor of Chemistry, Director of the High Temperature Materials Laboratory.

In April, 2000 John L. Zimmerman has defended a Ph. D. Thesis titled "Chemistry of Nanoscale Carbon Materials: Gas-Phase Purification of Single-Wall Carbon Nanotubes, Synthesis of Nanoscale Carbon Nitrides, and Nanodiamonds in Meteorite Carbon with Related Diamond Surface Chemistry".

(8) REPORT OF INVENTIONS

Solid State Synthesis of Carbon Nitride. V. N. Khabashesku and J. L. Margrave, Invention disclosure. Provisional patent issued on July 27, **1999.**

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(10) APPENDIXES

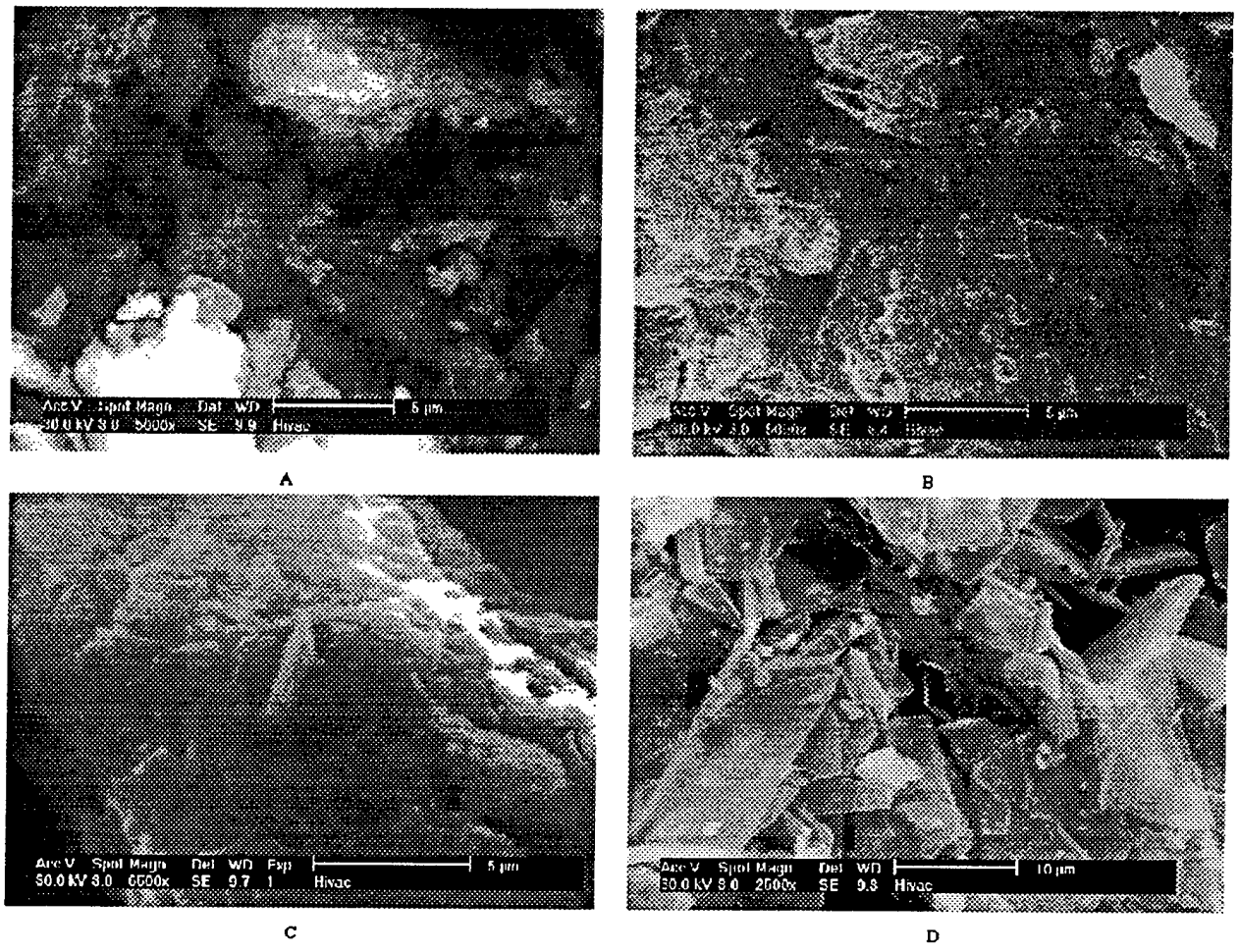

Figure 1. Scanning electron micrographs: **A** - a-C_3N_4 powder precursor, **B** - densified material obtained after exposure of powder to high pressure of 8 Gpa at room temperature, **C** - the material obtained from powder after exposure to high pressure of 12 Gpa at temperature of 400 °C; **D** - pure carbon graphite material formed from powder after exposure to high pressure of 8 Gpa at temperature of 1200 °C.

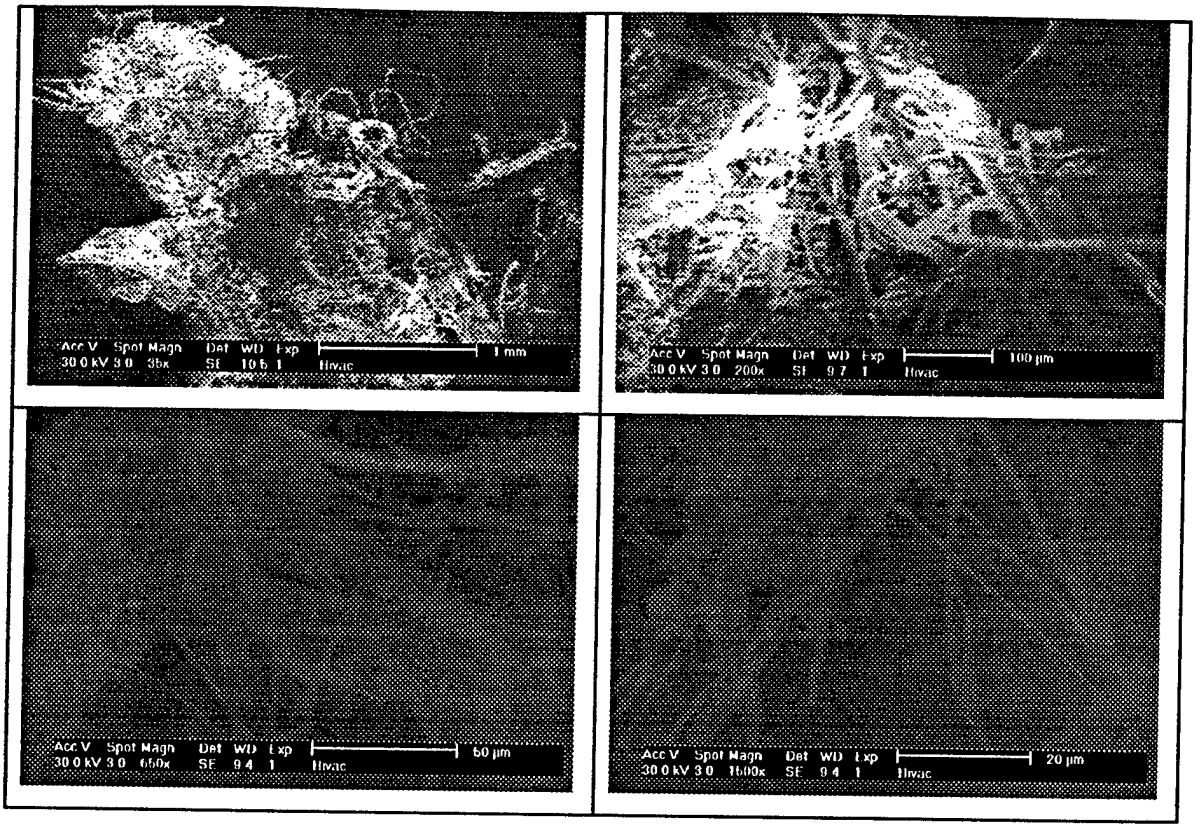

Figure 2. Scanning Electron Micrographs of B-C-N Fibers Grown on Ni-foil Surface.

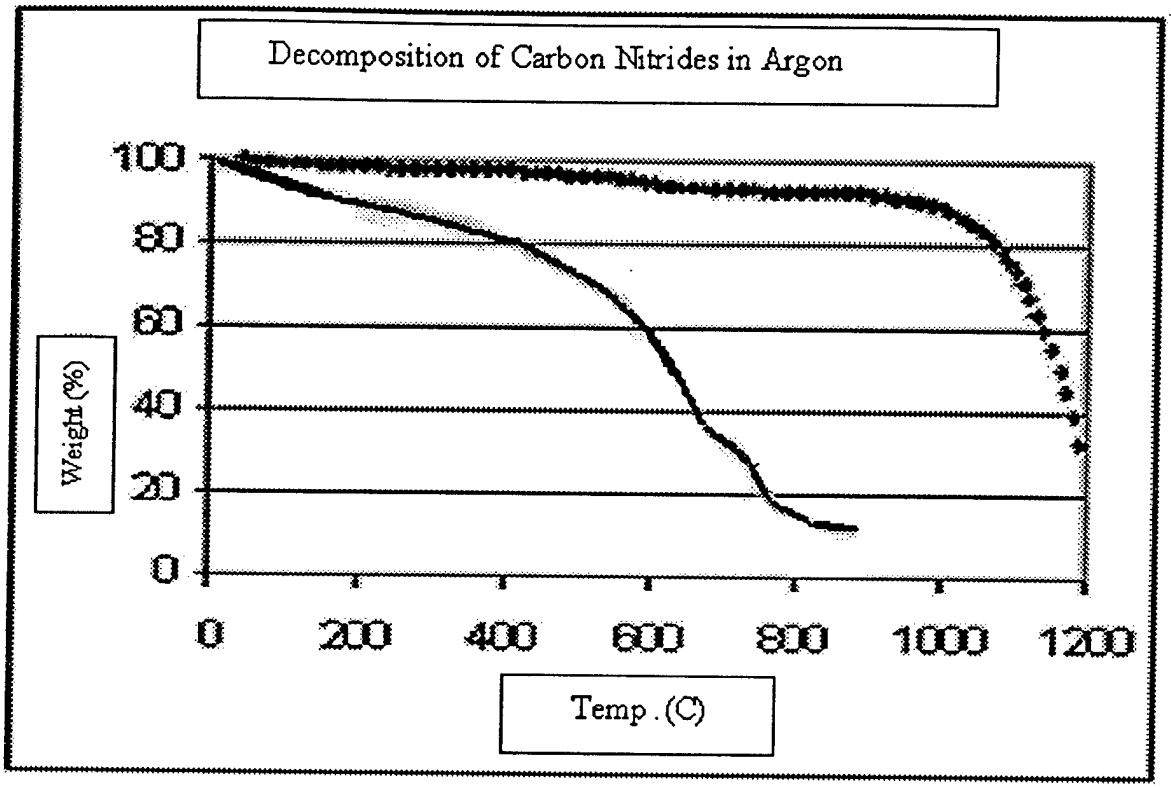

Figure 3. TGA data plots for B-C-N (top) and C_3N_4 (bottom) amorphous materials.

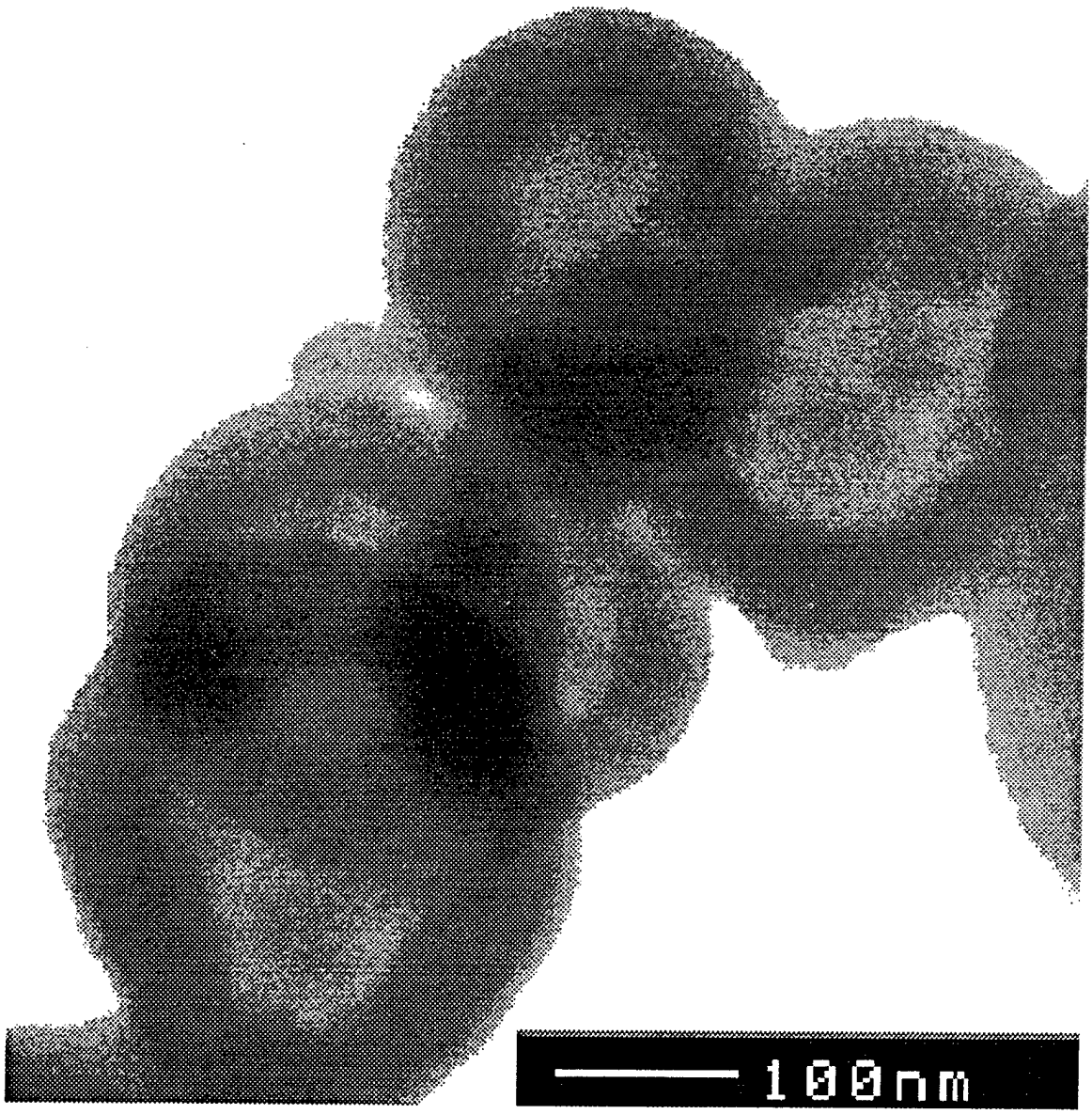

Figure 4. Transmission Electron Microscopy Image of Hollow Nanoscale Carbon Nitride Spherical Particles