Carbon Nitrides

Preparation of Nitrogen-Rich Nanolayered, Nanoclustered, and Nanodendritic Carbon Nitrides**

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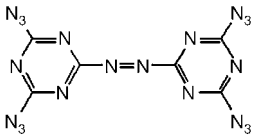
Carbon nitrides are of current interest due to their novel mechanical, optical, and tribological properties including low density, surface roughness, wear resistance, chemical inertness, and biocompatibility.[1–4] These superhard diamondlike materials promise a variety of technological and biological applications, for example, biocompatible coatings on biomedical implants,[5–6] battery electrodes,[7–8] gas-separation systems,[9] corrosion protection,[10] and humidity and gas sensors.[11] As these applications are primarily governed by the particle size, material texture, and nitrogen content, an extensive effort has focused on the discovery of precursors along with appropriate methods to control the size, regulate the texture, and increase the nitrogen content of carbon nitrides. We report here three novel nitrogen-rich nanolayered, nanoclustered, and nanodendritic carbon nitrides that were prepared from 4,4′,6,6′-tetra(azido)azo-1,3,5-triazine (TAAT), a member of a unique class of high-nitrogen C,N-containing energetic materials.



TAAT
m.p. 200 °C (decomp.)

Gillan reported the preparation of single-textural carbon nitrides C_3N_4 (60.9 wt % N, $\rho = 1.82\ g\,cm^{-3}$) and C_3N_5 (66.0 wt % N, $\rho = 1.82\ g\,cm^{-3}$) by pyrolyses of 2,4,6-tri-(azido)-1,3,5-triazine (TAT) at 85 °C.[12] Although pressurization was not required for making C_3N_4, 6 atm of N_2 was needed in the preparation of C_3N_5. Other preparative methods using 1,3,5-triazine-[4,13,14] and 2,5,8-heptazine-based[3,15–17] compounds as precursors have involved either applied pressure, high temperature, shock compression, or combinations of at least two of these conditions; however, the products obtained were nitrogen-poor materials, occasionally contaminated with hydrogen-incorporating byproducts. Our preparative protocols using TAAT yield three novel morphologies of nitrogen-rich carbon nitrides C_2N_3 (63.6 wt % N, $\rho = 1.32 \pm 0.01\ g\,cm^{-3}$) and C_3N_5 (66.0 wt % N, $\rho = 0.44 \pm 0.01$ and $1.08 \pm 0.01\ g\,cm^{-3}$). The pyrolyses are simple, occur under mild conditions (i.e., low temperature and without applied pressure), and require no vacuum systems, extraction, carbonization, or purification. TAAT was proposed as one of the intermediates in the decomposition of TAT,[12] and we recently developed a three-step synthetic pathway for this material.[18]

Nitrogen-rich C_2N_3 was prepared under a nitrogen atmosphere.[19] A 1.0 g crystalline sample of TAAT was loaded into a 50-mL stainless steel bomb, which was heated to 160 °C over 3 h and held at this temperature for an additional 4 h. The temperature was then increased to 185 °C over 5 h and maintained at this temperature overnight to yield glassy nanolayered C_2N_3 carbon nitride with a density of $1.32 \pm 0.01\ g\,cm^{-3}$. The glassy nanolayer was characterized by IR spectroscopy, gas pycnometry (GP), elemental analysis, thermogravimetric analysis (TGA),[20] and SEM imaging (Figure 1).

The interlinked three-dimensional network of glassy pockets shown in Figure 1 (right) suggested that the conversion to C_2N_3 involved a series of phase transitions (i.e., plastic, liquid, and solid). When the temperature was first raised from room temperature to 160 °C, TAAT became viscous, as indicated by the plastic property illustrated in Figure 2, and then gradually liquefied as the temperature approached 185 °C. The softening of TAAT to a viscous liquid

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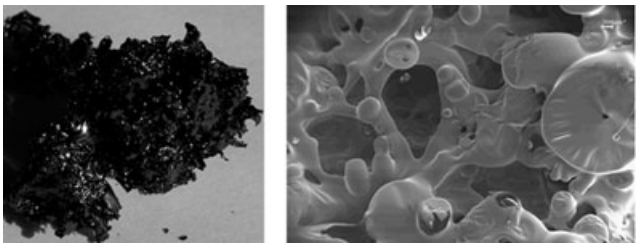

Figure 1. Glassy nanolayered C_2N_3: Photograph (left) and SEM image (×16000, right).

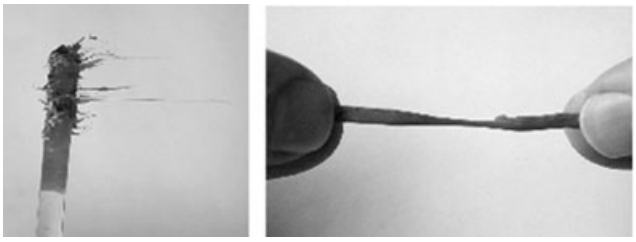

Figure 2. Photographs of TAAT with a trace of chloroform.

at 150 °C can be visually observed by using a Mel-Temp apparatus.

At 185 °C, liquid TAAT slowly decomposed to form glassy nanolayered carbon nitride, presumably by extrusion of nitrogen gas that was trapped inside the product. Slow release of the nitrogen gas over an extended period results in pockets interconnected by gossamer tunnels (Figure 1, right). From our previous study,[18] TAAT is a viscous material either at a temperature of 150 °C or when a trace of solvent remains in the sample. This plastic property makes TAAT the unique precursor for glassy nanolayered carbon nitride.

Nitrogen-rich C_3N_5 was prepared by two different heating protocols in the 50-mL stainless steel bomb. Under a nitrogen atmosphere, 1.0 g of crystalline TAAT was heated to 160 °C over 3 h and held at that temperature for an additional 4 h. The temperature was then increased to 200 °C over 5 h and maintained at this temperature overnight to produce a very low density carbon nitride ($\rho = 0.44 \pm 0.01\ g\,cm^{-3}$) with a novel tunnel-like structure constituted of spherical/elliptical nanoclusters. This nanoclustered C_3N_5 carbon nitride was characterized by IR spectroscopy, GP, elemental analysis, TGA,[21] and SEM imaging (see Figure 3).

During the course of heating for 4 h at 160 °C followed by 5 h at 200 °C, crystalline TAAT underwent a phase change from viscous plastic to liquid. At 200 °C, the liquefied TAAT

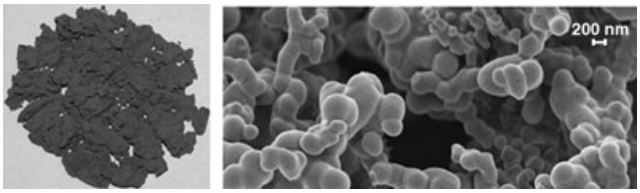

Figure 3. Spherical/elliptical nanoclustered C_3N_5: Photograph (left) and SEM image (×10000, right).

decomposed to give spherical/elliptical nanoclusters and nitrogen gas as byproduct. This suggested that the relatively slow decomposition had thrust nitrogen gas directly into the winding hollow tunnels.

In the second heating protocol, the crystalline TAAT was heated to 205 °C over 4 h and then maintained at this temperature overnight. The unprecedented denser nanodendritic C_3N_5 carbon nitride ($\rho = 1.08 \pm 0.01\ g\,cm^{-3}$) was obtained. Interlinked segments whose diameters ranged from 10 to 100 nm were characterized by IR spectroscopy, GP, elemental analysis, TGA,[22] and SEM imaging (Figure 4).

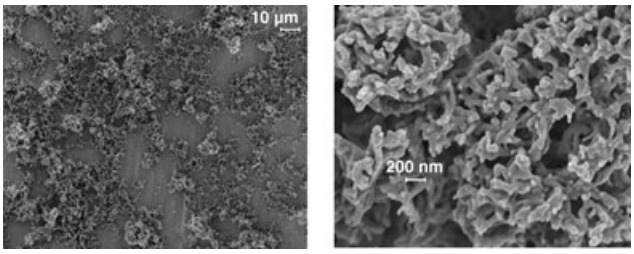

Figure 4. SEM images of nanodendritic C_3N_5: ×500 (left) and ×20000 (right).

During the period of four hours heating from room temperature to 205 °C, rapid release of N_2 from crystalline TAAT was accompanied by conversion of TAAT into an irregular framework of interlocking fragments without completely undergoing any phase transition. This faster decomposition gave a nearly $2^1/_2$-times denser C_3N_5 with much smaller particle sizes.

Unlike many other organic compounds, such as mesocarbon microbeads,[23,24] mesophase pitch-based carbon fibers,[25–27] non-azido-substituted triazines[4,13,14] and non-azido-substituted heptazines,[3,15–17] TAAT[18] and other polyazido compounds containing only C and N atoms[28,29] are ideal precursors for nitrogen-rich carbon nitrides because of their clean and thermodynamically favorable decomposition, which presumably extrudes nitrogen gas as the only byproduct [Eqs. (1) and (2)].

$$C_6N_{20} \xrightarrow{\Delta} 3\,C_2N_3 + 5.5\,N_2 \quad (1)$$

$$C_6N_{20} \xrightarrow{\Delta} 2\,C_3N_5 + 5\,N_2 \quad (2)$$

The glassy/sturdy C_2N_3 carbon nitride in Figure 1 and the powder/soft C_3N_5 carbon nitrides in Figures 3 and 4 have revealed that the textures, nitrogen contents, and densities of these nitrogen-rich carbon nitrides are highly dependent on the temperatures at which decomposition occurs. The nanoclusters in Figure 3 and the nanodendrites in Figure 4 have shown that the morphologies of C_3N_5 are governed by the heating patterns, while the sizes of nanoparticles are inversely proportional to the heating time. The pyrolyses of TAAT to three novel nitrogen-rich carbon nitrides have illustrated that mutual manipulation of the unique viscosity and rate of

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decomposition played an essential role in controlling the nature of the pyrolized products.

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[19] All preparations were carried out at an initial atmospheric pressure of 580 torr (11.2 psi or 0.76 atm) and a relative humidity of less than 15% at Los Alamos (New Mexico, USA) at an elevation of 7500 ft. Preparation of each type of carbon nitride was repeated in triplicate with temperatures maintained within ±2 °C.
[20] Characterization of glassy nanolayered C_2N_3: IR (Nujol): $\tilde{\nu}$ = 1456 (vs), 1367 (vs), 1342 (vs), 1303 (vs), 1080 (vs), 848 (s), 804 (vs), 398 cm^{-1} (vs), presumably due to aromatic ring modes and aromatic C–N and C–C bonds; GP: $\rho = 1.32 \pm 0.01\ g\,cm^{-3}$; elemental analysis (%): found: C 36.34, H 0.58, N, 63.07; TGA: robust up to ca. 670 °C.
[21] Characterization of nanoclustered C_3N_5 carbon nitride: IR (Nujol): $\tilde{\nu}$ = 1641 (vs), 1565 (vs), 1461 (vs), 1307 (vs), 1244 (vs), 968 (s), 814 (vs), 374 cm^{-1} (vs), presumably due to conjugated C=N/C=C species, aromatic ring modes, and aromatic C–N and C–C bonds; GP: $\rho = 0.44 \pm 0.01\ g\,cm^{-3}$; elemental analysis (%): found: C 33.18, H 0.63, N 65.89; TGA: robust up to ca. 650 °C.
[22] Characterization of nanodendritic C_3N_5 carbon nitride: IR (Nujol): $\tilde{\nu}$ = 1640 (vs), 1564 (vs), 1461 (vs), 1304 (vs), 1246 (vs), 968 (s), 815 (vs), 378 cm^{-1} (vs), presumably due to conjugated C=N/C=C species, aromatic ring modes, and aromatic C–N and C–C bonds; GP: $\rho = 1.08 \pm 0.01\ g\,cm^{-3}$; elemental analysis (%): found: C 33.26, H 0.29, N 65.70; TGA: robust up to ca. 650 °C.
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