

The Combustion Properties of Novel High-Nitrogen Energetic Materials

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Abstract: *High-nitrogen energetic materials based on the tetrazine and tetrazole ring systems have shown unique and unpredictable combustion behavior. Unlike traditional energetic compounds, such as 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), which derive their energy by the oxidation of the carbon and hydrogen skeletal atoms by the oxygen carrying nitro group, high-nitrogen materials typically have large positive heats of formation as their source of energy. This difference in the energy source may partly explain why the combustion chemistries of some high-nitrogen materials are unusual.*

Using the precursor 3,6-bis-(3,5-dimethylpyrazol-1-yl)-s-tetrazine (BDT), several useful energetic compounds based on the s-tetrazine system have been synthesized and studied. A number of these tetrazine-based materials have shown to exhibit burn rates with low sensitivity to pressure, namely 3,6-bis(1H-1,2,3,4-tetrazol-5-ylamino)-s-tetrazine (BTATz), 3,6-bis-nitroguanyl-1,2,4,5-tetrazine (NQ₂Tz), the corresponding bis-triaminoguanidinium salt (TAG₂NQ₂Tz) and the N-oxides of 3,3'-azobis(6-amino-1,2,4,5-tetrazine) (DAATO3.5). A fifth compound of high nitrogen make-up, triaminoguanidinium azotetrazolate (TAGzT), is not prepared from BDT, but it also burns at exceptional rates with low pressure sensitivity.

The tetrazole-based materials, bis-(1(2)H-tetrazol-5-yl)-amine (BTA) and 5,5'-bis-1H-tetrazole (BT), are useful high-nitrogen energetic ligands for the preparation of metal complexes. While BTA, BT and their salts have been previously shown as possible energetic fuels for low-smoke pyrotechnic applications, some recent combustion experiments with the metal complexes of BT and BTA have proved to be even more noteworthy. These metal ion complexes have sufficient internal energy that they can burn under an inert atmosphere to produce the free metal, usually in the form of high-surface area foams or nano-sized particles. This highly unusual, reductive combustion chemistry may lead to efficient and controlled production of metal nanofoams.

The heat of formation (ΔH_f) of 3,6-diazo-1,2,4,5-tetrazine (DiAT), a highly energetic and sensitive energetic material (most notably to friction, spark and impact), was calculated to be approximately +1100 kJ mol⁻¹, or +92 kJ mol-atom⁻¹, using an additive method. Depending on the heating rate, DiAT can undergo pyrolytic decomposition to produce either carbon nanospheres or carbon nitride nanopolygons. With slow heating, leaf-like or rope-like forms of carbon nitride were the predominant products. With faster heating, carbon spheres with diameters on the order of 10 to 100 nm were produced. Such nanomaterials are of interest to the scientific community for a wide number of industrial applications.

Keywords: *high-nitrogen, tetrazole, tetrazine, combustion, nanomaterials, propellant, foam*

Introduction

At Los Alamos National Laboratory we have developed a number of energetic high-nitrogen

materials that exhibit unusual combustion properties with a variety of potential commercial and military applications. These materials have two characteristic attributes. First, they are

high in nitrogen and, consequently, have large positive heats of formation, which is attributed to the nitrogen–nitrogen bonds that are prevalent in these systems.¹ Second, because the skeletal framework contains relatively less carbon and hydrogen when compared to traditional explosives, the oxygen balance can be more easily achieved. Furthermore, these materials possess relatively high crystal densities, a critical parameter for the enhancement of explosive performance, and are often insensitive towards destructive stimuli such as impact, friction, and electrostatic discharge. Of particular interest to our group is the synthesis of high-nitrogen materials based on the tetrazine and the tetrazole systems. In this paper we describe the combustion properties of a number of these materials in three applications, specifically their potential use as high-performance propellant ingredients, precursors for high-surface area and low-density metal foams, and carbon and carbon nitride nanomaterials.

High-Performance Propellant Ingredients

Solid propellants provide a means of converting chemical potential energy into useful kinetic energy. Although the chemical ingredients of propellants are varied and complex, two basic components—fuel and oxidizer—burn to produce heat and gas, which can expand in a gun barrel to push a shell, or flow at supersonic speed in a De Laval nozzle to provide thrust. High-nitrogen compounds may be the key to meeting the advanced performance objectives of next-generation propellants. Classical solid propellants have not changed fundamentally for nearly three decades and can be separated into two general classes. **Monopropellants** contain ingredients that have fuel and oxidizer in the same molecule, such as the explosives octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) or nitroglycerine (NG). **Heterogeneous** or **composite propellants** are aggregate mixtures of fuel and oxidizer bound together by polymeric binder, which is a fuel itself. The ammonium perchlorate (AP) and hydroxy-terminated polybutadiene (HTPB) matrix is a popular composite motor propellant system. Ingredients, such as HMX, aluminum or AP of different particle sizes, are often included in the composite matrix to enhance or tailor its

performance. A serious drawback of AP solid propellants, however, is the copious amount of toxic hydrogen chloride that is generated as a combustion product. One solid rocket booster of the space shuttle, for example, generates 240,000 pounds (109 tonnes) of hydrogen chloride gas.

High-nitrogen energetic materials offer the possibility of significant performance improvement over current propellant systems in at least two ways. In one, inert and invisible nitrogen gas is the major combustion product of high-nitrogen materials, which is a clear improvement over toxic hydrogen chloride produced by AP composite propellants. This will also facilitate the formulation of low-smoke, “reduced-signature” propellants, a useful feature that increases the defensive posture of an attacker. In the second, high-nitrogen materials typically have large positive heats of formation and generate low molecular weight gases, attributes that are very desirable for high impulse performance. This is best exemplified by the simplified reciprocal relationship between the exit gas velocity, V , of a De Laval nozzle and the mean average of the molecular weights of the combustion gas products, M_{ave} .

$$V \propto [1/M_{\text{ave}}]^{1/2}$$

Decreasing the overall molecular weight of the exit gases by substituting hydrogen chloride, carbon monoxide and carbon dioxide, which are typical reaction products of HMX/AP composite motors, with lighter gases of high-nitrogen compounds, such as H_2 and N_2 , will increase the exit gas velocity, and in turn the impulse of the motor.

In this section, we compare the burn-rate data of five high-nitrogen energetic materials as viable candidates for use in high-performance propellants. They are: (1) 3,6-bis(1*H*-1,2,3,4-tetrazol-5-ylamino)-*s*-tetrazine (BTATz), (2) the mixed *N*-oxides of 3,3'-azobis(6-amino-1,2,4,5-tetrazine) (DAATO3.5), (3) triaminoguanidinium azotetrazolate (TAGzT), (4) 3,6-bis-nitroguanyl-1,2,4,5-tetrazine (NQ₂Tz), and (5) its corresponding bis-triaminoguanidinium salt (TAG₂NQ₂Tz). The structures of these materials are given in Figure 1. Except for TAGzT, all of the above compounds are derived from the valuable precursor, 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine, which is prepared in two steps from commercially available triaminoguanidine hydrochloride,

2,4-pentanedione, and nitrogen dioxide.² The synthesis procedures of these five materials have been described elsewhere.³

In Figure 2, the measured burn rate *vs.* pressure profiles are graphically represented for the pressure ranges studied for each material.⁴ The linear relationship between burn rate (r_b) and pressure (p) is best described by the empirical equation $r_b = cp^n$, where c is the empirical constant and n is the pressure exponent.⁵ A large pressure exponent (approaching 1 or greater) is often typical with traditional high explosive materials and indicates that 2nd order gas-phase reactions dominate the combustion process. A lower pressure exponent, however, is attributed to early rate-controlling reactions in the condensed phase, and thus results in a burn rate that is insensitive to changes in pressure. Low pressure sensitivity (*i.e.*, a low

pressure exponent) offers advantages in the design of gun and rocket propellants, particularly in motor stability. Conversely, energetic materials with high exponent values are typically avoided for use in propellant applications. In all five materials, the pressure exponents are reasonably, if not exceptionally low (see Table 1). For comparison, the pressure exponent for HMX is 0.75 and its burn rate at 1000 psi is 1.1 cm s^{-1} .⁵

Nanoporous metal foams

The synthesis of low-density, nanoporous materials has been an active area of study in chemistry and materials science dating back to the first synthesis of aerogels.⁶ These materials, however, are mostly limited to silica, metal oxides (*e.g.*, Al_2O_3) and organic aerogels (*e.g.*, resorcinol/formaldehyde), with the only elemental material being carbon, arising from the pyrolysis of organic aerogels.

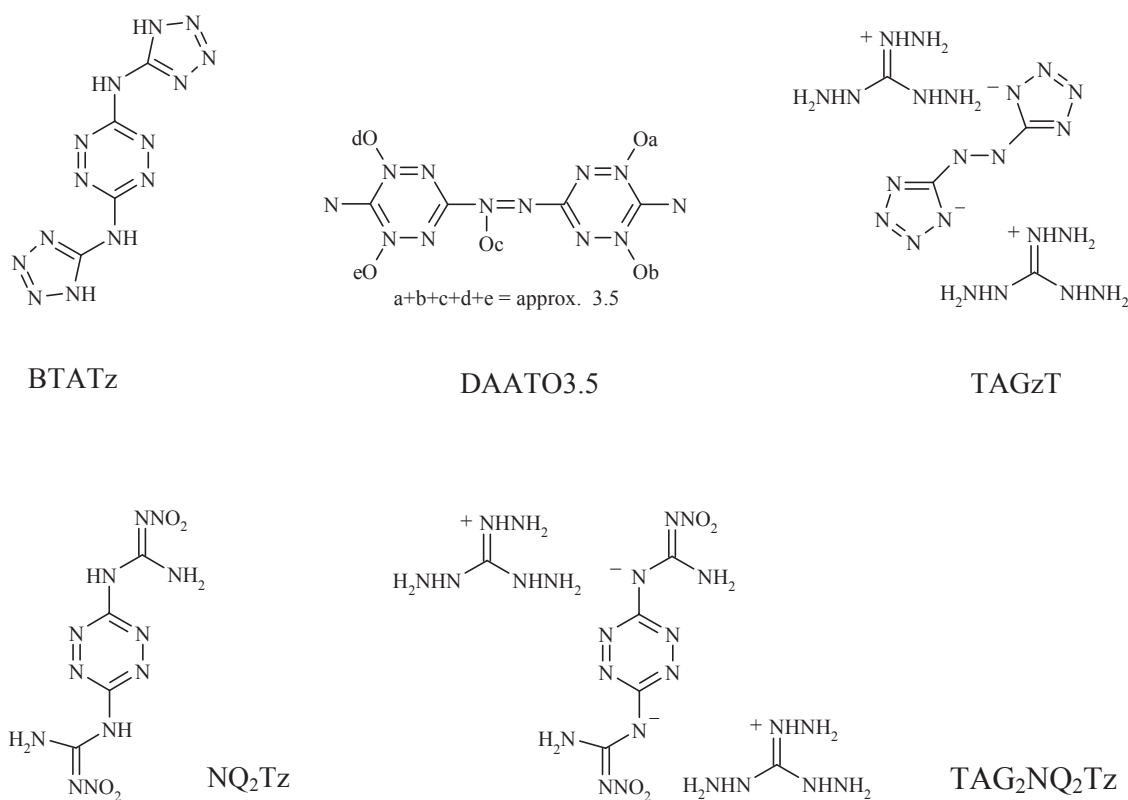


Figure 1 Five high-nitrogen energetic materials of interest as high-performance propellant additives: (a) 3,6-bis(1H-1,2,3,4-tetrazol-5-ylamino)-s-tetrazine (BTATz); (b) the mixed N-oxides of 3,3'-azobis(6-amino-1,2,4,5-tetrazine) (DAATO3.5); (c) triaminoguanidinium azotetrazolate (TAGzT); (d) 3,6-bis-nitroguanyl-1,2,4,5-tetrazine (NQ₂Tz); and (e) its corresponding bis-triaminoguanidinium salt (TAG₂NQ₂Tz).

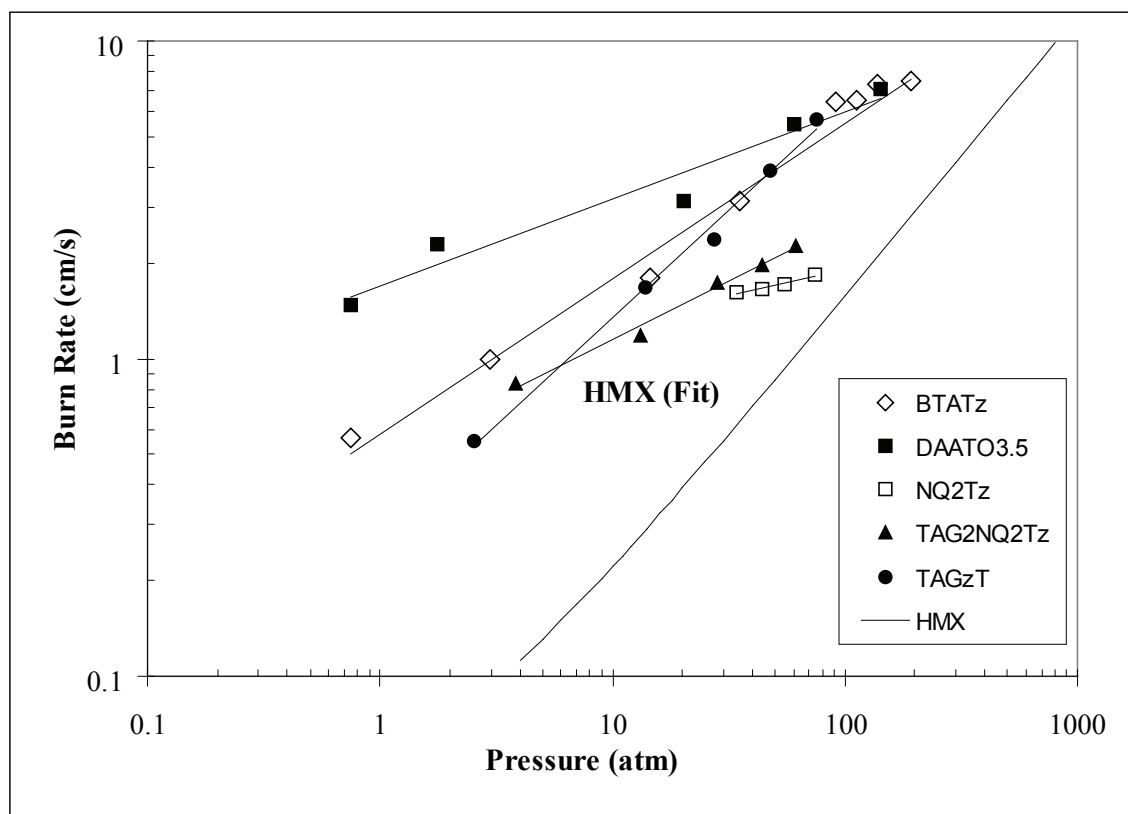


Figure 2 Burn rate versus pressure profile for five high-nitrogen energetic materials. Some of the materials were pressed with binders (BTATz with 3% Kel-F-800, DAATO3.5 with 5% PVA and 1% TEG), while the rest were studied as neat materials.

Table 1 Sensitivity and burn rate data for five high nitrogen materials. All data are for pure material unless noted otherwise.

	BTATz	DAATO3.5	TAGzT	NQ ₂ Tz	TAG ₂ NQ ₂ Tz
Pressure Exponent, <i>n</i>	0.49 ^a	0.275 ^b	0.67	0.163	0.366
Empirical Constant, <i>c</i>	0.581	1.69	0.287	0.899	0.494
Burn Rate at 1000 psi †	4.6	5.4	4.9	2.0	2.3
H ₅₀ (cm) Type 12	32 ^c	50	25	65	114
DSC Onset (°C)	264	177	195	228	166
Friction (kg) BAM	> 36	2-14	10	> 36	> 36
Spark (J)	< 0.36 ^d	< 0.36	< 0.31 ^e	> 0.36	> 0.36
Density (g cm ⁻¹)	1.76	1.88	1.60	1.76	1.61
Δ <i>H_f</i> (kJ mol ⁻¹)	+883	+690	+1075	+389	+1255
Δ <i>H_f</i> (kJ mol-atom ⁻¹)	+40.1	+29.4	+24.4	+15.0	+22.4

^aBTATz formulated with 3% Kel-F-800 binder. ^bDAATO3.5 formulated with 5% PVA and 1% TEG. ^cPositive impact results ranged widely between 32 and 200 cm so a conservative value of 32 cm was assigned. ^d11 out of 13 samples initiated when subjected to 0.36 J of energy. ^eThreshold Initiation Limit (TIL) value, which represents a probability that an event will happen 3.4% of the time a given stimulus is applied. † 68.0 atm or 6.89 MPa.

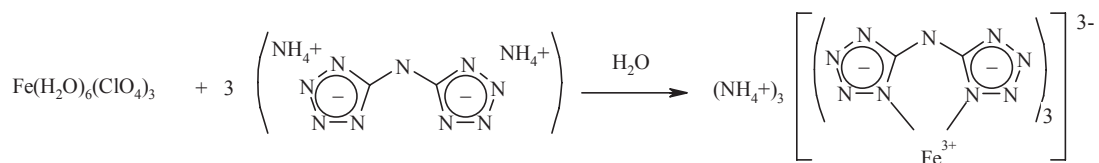


Figure 3 Synthesis scheme of Fe-BTA, formed by the reaction of iron(III) perchlorate with 3 equivalents of diammonium salt of bis-(1(2)H-tetrazol-5-yl)-amine (BTA).

A method to prepare ultra-low-density transition-metal foams has been developed using a novel pyrotechnic technique. The process is simple in concept; a transition-metal complex containing an energetic, high-nitrogen ligand is allowed to combust under an inert atmosphere, such as argon or nitrogen. As the complex burns, the metal

cation undergoes chemical reduction to the free metal. Because the intrinsic energy of the selected complex is high, the combustion is self-sustaining. By this method, metal monolithic foams with remarkably low densities (0.011 g cm^{-3}) and high surface areas ($258 \text{ m}^2 \text{ g}^{-1}$) have been formed. The ability to form monolithic metallic nanocellular

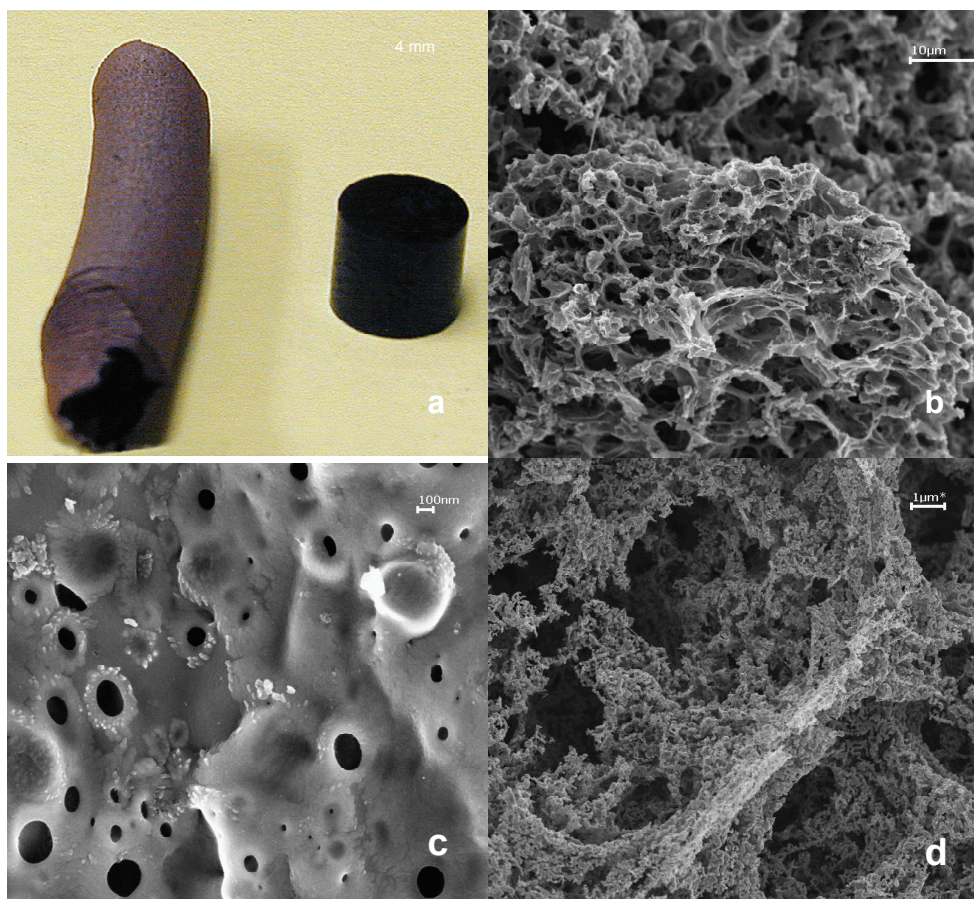


Figure 4 (a) Photograph, 4 mm scale, of iron foam next to unburned pellet of the Fe-BTA complex. (b) Scanning electron micrograph (SEM), 10 μm scale, of low pressure iron foam showing pore structure of roughly 1 μm. (c) SEM, 100 nm scale, of high pressure iron foam showing pore sub-structure of roughly 20–100 nm. (d) SEM, 1 μm scale, of heat-treated iron foam.

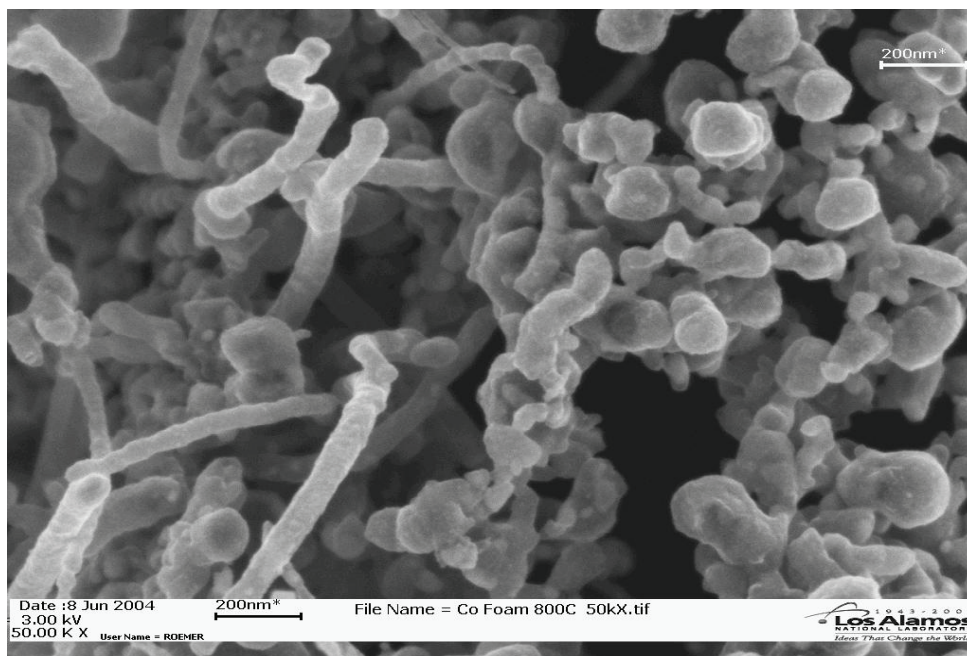


Figure 5 SEM, scale 200 nm, of Co foam after heat treatment, foam walls made up of particles and rods of cobalt metal.

porous materials is presently not possible using conventional processes, particularly at the densities we have observed or with such ease of production. To date, we have produced iron, cobalt, copper and silver foams from their corresponding high-nitrogen ligand complexes.

The lowest-density metal foams found in the literature range from 0.04-0.08 g cm⁻³ and were

made from magnesium and aluminum. These foams, however, contain cells on the millimetre length-scale, and have a relatively low surface area.⁷ Recently, a silver sponge was reported with pore sizes on the order of a few microns and a surface area of 0.5 m² g⁻¹, however, no density was given.⁸ The synthesis of dendritic platinum with three-dimensional foam-like nanostructures

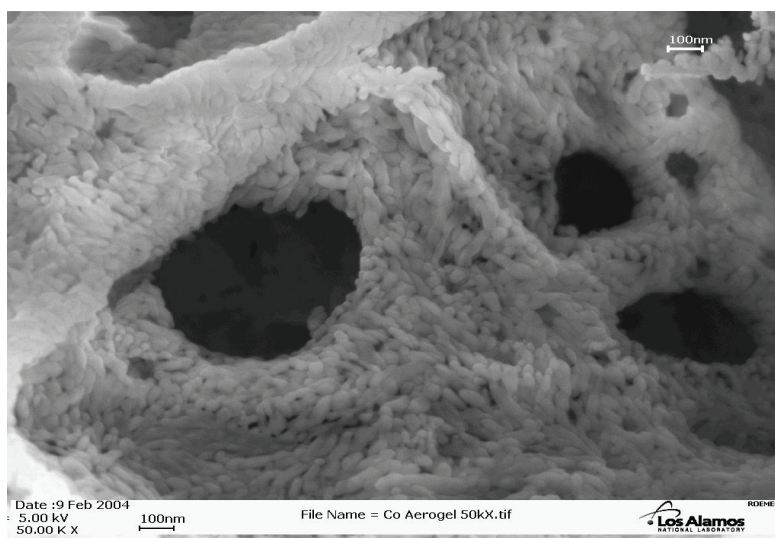


Figure 6 SEM, scale 100 nm, of Co foam showing nanoporous substructure made up of rice-like particles that form foam walls.

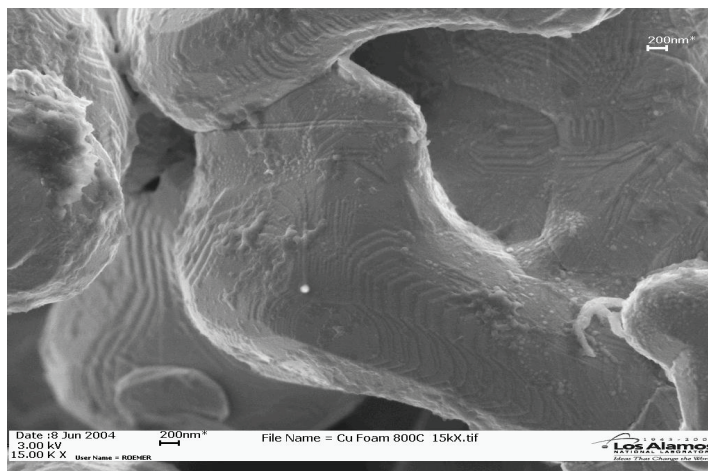


Figure 7 SEM, 200 nm scale, of heat-treated copper foam.

was also recently described, but the structures are limited to small clusters ranging in size from 6 to 200 nm.⁹

The first and best characterized metal foam in our initial studies was obtained from the ammonium tris(bi(tetrazolato)amine)ferrate(III) complex (Fe-BTA). This complex is easily formed by the reaction of 3 : 1 molar ratio of the diammonium salt of bis-(1(2)*H*-tetrazol-5-yl)-amine (BTA) and iron(III) perchlorate (Figure 3). BTA is a

high-nitrogen material easily synthesized from inexpensive sodium dicyanamide and sodium azide under controlled addition of hydrochloric acid.¹⁰ When ignited as a loose powder in air, Fe-BTA rapidly combusts with the production of orange sparks, which is attributed to nascent, elemental iron burning. The combustion of cylindrical pellets of Fe-BTA in a combustion chamber of inert atmosphere at varying pressures results in the formation of the metal foam monolith

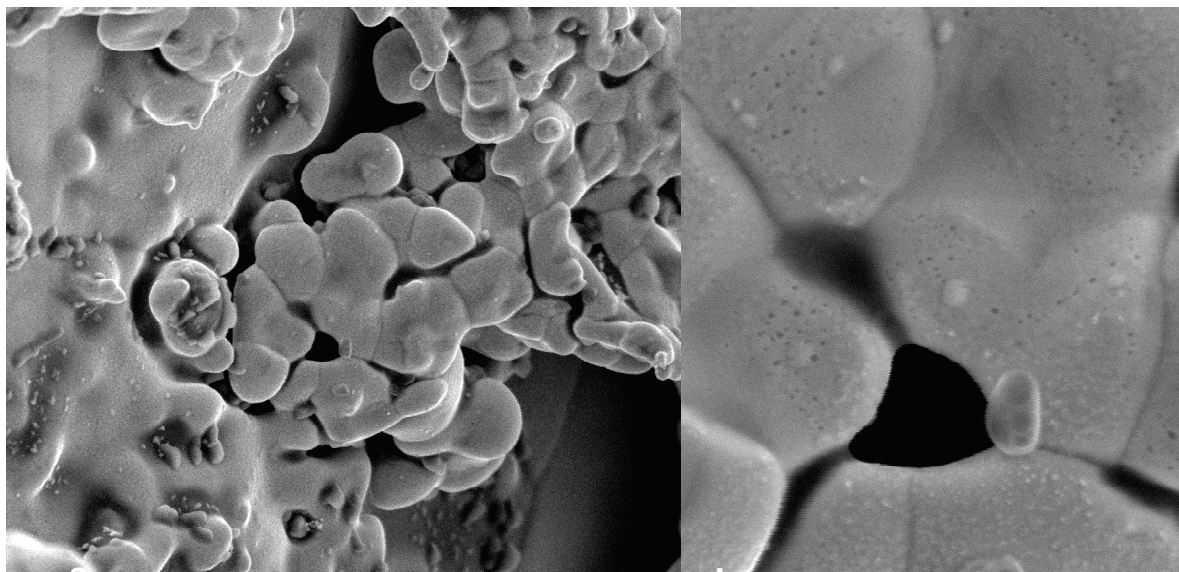


Figure 8 (a) SEM, scale 1 μm, of Ag foam. (b) scale 100 nm, closer view of (a) showing surface nanoporosity of around 20 nm.

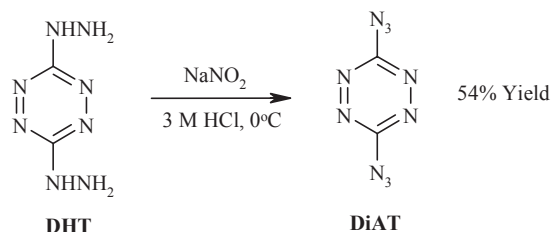


Figure 9 Synthesis scheme for DiAT from 3,6-dihydrazino-1,2,4,5-tetrazine (DHT).

(Figure 4a). Following combustion at 20.4 atm, a bimodal pore size distribution was observed within the micron and 20–200 nm ranges. Interestingly, combustion at higher pressure (72.3 atm) resulted in a metallic foam containing only the 20–200 nm pore size distribution (Figures 4b–c). Brunauer–Emmett–Teller (BET) surface area analysis for the metal foam produced at 20.4 atm yielded an extraordinarily high surface area of 258 m g⁻¹. For comparison, a high surface area titania aerogel has BET values that range from 100 to 200 m g⁻¹.¹¹ BET surface areas for foams produced at higher pressures (*ca.* 70 atm) range from 12 to 17 m g⁻¹. Evidently, the high-nitrogen ligand acted as a blowing agent on a molecular level as Fe-BTA decomposed, liberating decomposition gases. Elemental analysis (standard combustion technique) and energy dispersive spectra (EDS) demonstrated that the as-produced metal foams contain up to 50% carbon and nitrogen which are mostly removed by heating to 1073 K in an inert atmosphere (Figure 4d). While no density or surface area measurements were made on the heat-treated foam due to small sample size, it is apparent from the SEM image that no sintering took place (Figures 4d and 5). Thermogravimetric analysis (TGA) and EDS indicate that the heat-treated foams range from 10% remaining carbon

(iron foam) to essentially pure (copper foam).

Metal foam production using this unique combustion method is possible with other transition metal complexes. Cobalt, silver and copper metal foams have been produced from the corresponding BTA complexes; however, the morphology of the resultant foam is strongly dependent on the metal employed. Electron micrographs of the cobalt foam showed the two basic pore morphologies observed in the iron foam. A third morphology consisting of small cobalt grains (*ca.* 100 nm) that aggregate to form the foam walls, which should dramatically increase the surface area of the metal foam (Figure 6). The copper foam was of a higher density and had much more regular, yet larger pore sizes of approximately 1 micron, and after heating to remove impurities, displayed interesting crystal lattice lines along the foam walls (Figure 7). The silver foam was the most dense, and in fact had partially fused to form shiny silver beads. Selected SEM images of the silver foam that had not fused show a foam structure, indicating that monoliths similar to those of iron foam could perhaps be achieved by optimizing the combustion method (Figures 8a–b). This pyrotechnic method shows promise as a flexible and simple approach to the formation of a wide range of new nanoporous metals that are not currently accessible by state-of-

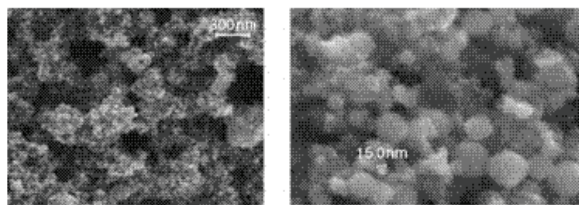


Figure 10 SEM images of carbon nanospheres at magnifications of 25,000 × (left) and 150,000 × (right).

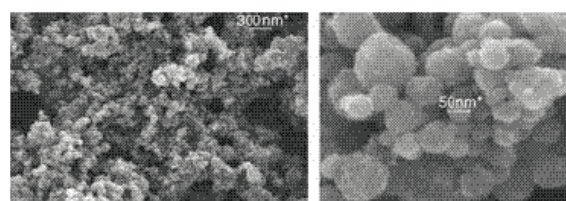


Figure 11 SEM images of carbon nanopolygons at magnifications of 25,000 × (left) and 150,000 × (right).

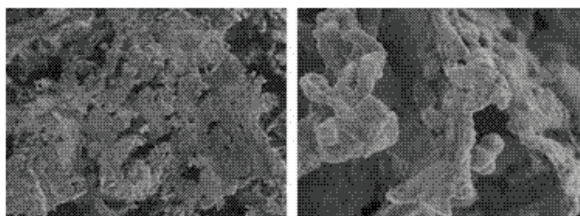


Figure 12 SEM images of carbon nitride, C_3N_4 , with leaf-like (left) and rope-like (right) morphologies.

the-art nanoscience. Possible applications abound in the fields of catalysis, fuel cells, hydrogen storage, unique insulation, and electromagnetic absorption materials.

Pyrolysis of 3,6-diazido-s-tetrazine (DiAT)

The compound, 3,6-diazido-1,2,4,5-tetrazine (DiAT), is easily prepared by the diazotization of 3,6-dihydrazino-1,2,4,5-tetrazine (DHT) (Figure 9). *Typical of organic azides, DiAT is extremely sensitive to spark, friction and impact stimuli and must be handled with extreme care and in small quantities, preferably stored as a solution.*¹² Using the additive method, the heat of formation of DiAT was estimated to be relatively high, approximately $+1100 \text{ kJ mol}^{-1}$, or $+92 \text{ kJ mol-atom}^{-1}$.¹³ The large positive value is attributed to its high nitrogen makeup of 85.4% by weight. Because of these attributes, DiAT was examined as a precursor for the production of carbon and carbon nitride nanomaterials by pyrolytic methods.

Elemental carbon is used in many applications, including high-density and high-strength carbon artifacts, super-active carbon beads of high surface area, lithium storage, lithium battery anodes,

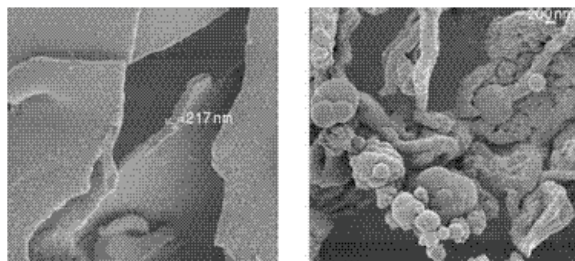


Figure 13 SEM images of higher-nitrogen content carbon nitride, C_3N_5 , with sheet-like (left) and rope and ball (right) morphologies.

spherical packing materials for HPLC, hydrogen storage applications, and catalysis.¹⁴ Because their applications significantly depend on the shape and size of the particles, much attention is focused on methods of preparation and characterization.

Besides carbon, carbon nitrides are also of interest to the materials community due to their novel mechanical, optical, and tribological properties, including low density, extreme hardness, surface roughness, wear resistance, chemical inertness, and biocompatibility. These mechanically hard materials promise a variety of technological and biological applications. For example, they are used as biocompatible coatings on biomedical implants, battery electrodes, catalytic supports, gas separation systems, electronic materials, and humidity and gas sensors.¹⁵ Applications of carbon nitrides are not only governed by the texture and size of the particles but also by the relative nitrogen content. As a consequence, extensive effort is focused on the discovery of precursors along with the appropriate methods to increase the nitrogen content in carbon nitrides.

Carbon nanoparticles were prepared by the pyrolytic decomposition of DiAT under atmospheric air. The reactions were carried out in a 50 mL heavy-walled pressure bomb. For ease and safety of handling fairly large quantities of DiAT, a method of loading the pressure bomb was developed. A chloroform solution containing 0.2 g of DiAT was poured into the bottom half of the bomb and the solvent allowed to evaporate in the hood. The bomb was assembled and then ramp-heated at a constant rate for 2 hours until the temperature reached $150 \text{ }^\circ\text{C}$. The bomb was cooled and disassembled and the resulting fine product collected from the walls. Elemental and SEM analysis confirmed the production of carbon nanospheres with diameters ranging from 25 to 100 nm (Figure 10). When the reaction was repeated, but with the heating accelerated such that $150 \text{ }^\circ\text{C}$ was reached within 1 hour, an audible pop within the pressure bomb was heard. Elemental analysis indicated that the resulting pyrolytic product was again mainly carbon. An SEM image revealed carbon nanospheres with larger diameters, ranging from 50 to 200 nm in diameter (Figure 11).

Nitrogen-rich carbon nitrides were produced

from DiAT when two different heating protocols were employed. Using the same pressure bomb and under ambient air pressure, DiAT (0.3 g) was heated to 100 °C over the course of 2 h and held at this temperature for an additional 4 h. The temperature was then increased to 150 °C over 3 h and maintained overnight to yield leaf-like carbon nitride C₃N₄ (Figure 12, left). When DiAT was heated to 150 °C over the course of 5 h and then held at that temperature overnight, carbon nitride C₃N₄ with a rope and ball morphology was obtained (Figure 12, right). The carbon nitride products from both reactions were confirmed by IR spectroscopy and elemental analysis. Carbon nitrides with higher nitrogen content were formed when the same two heating protocols as describe above were used but conducted under a nitrogen atmosphere. As measured by elemental analysis, the nitrogen content of the reaction products increased from C₃N₄ to C₃N₅. The SEM images of these nitrides show sheet-like (Figure 13, left) and rope and ball morphologies (Figure 13, right).

These results demonstrate a novel method of producing carbon nanospheres with diameters ranging from 5 to 50 nm and nitrogen-rich carbon nitrides of varying morphologies. While DiAT may be one possible precursor, other high-nitrogen compounds with high positive heats of formation may provide additional avenues for the synthesis of exotic carbon and carbon nitride nanomaterials.

Acknowledgements

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