

Barochemistry to Multifunctional High Energy Density Solid: Extended Phases of N₂, CO, and N₂+CO at High Pressures

Choong-Shik Yoo

Department of Chemistry and Institute for Shock Physics and, Washington State University, Pullman, WA 99164, U.S.A.

ABSTRACT

Many simple diatomic and triatomic molecules such as N₂ and CO₂ have the potential to form extended “polymeric” solids under extreme conditions, which can store a large sum of chemical energy in its three-dimensional network structures made of strong covalent bonds. Diatomic nitrogen is particularly of interest because of the uniquely large energy difference between that of the single bond (160 kJ/mol) and that of the triple bond (954 kJ/mol). As such, the transformation of a singly bonded polymeric nitrogen back to triply-bonded diatomic nitrogen molecules can release nearly 5 times the energy of TNT without any negative environmental impact. In this paper, we will describe our recent research efforts to synthesize novel extended phases of isoelectronic systems of N₂ and CO, as well as those of N₂+CO mixtures to lower the transition pressures and enhance the stability of recovered products at ambient condition.

INTRODUCTION

Despite great advances in research over many decades, today’s energetic materials are in low density, of low material strength, and are highly sensitive to shock. They burn incompletely, degrade, and age. These characteristics arise from low-dimensional open molecular structures with voids, grain boundaries, and defects. Overcoming these limitations is one of the grand challenges of our time. It will require development of structurally advanced energetic materials such as diamond-like extended solids in monolithic three-dimensional (3D) network structures in high density (~3 g/cc) and high-energy (~10 eV/nm) states without chemical heterogeneities or structural defects (Figure 1).

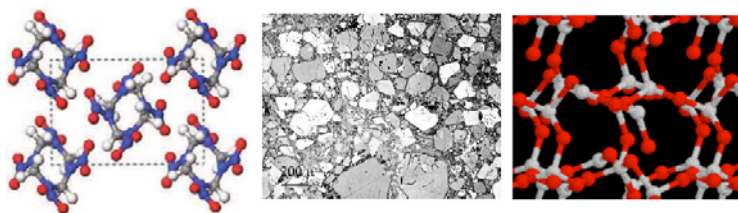


Figure 1. Structures of energetic materials: HMX with a large (~90%) empty space, a composite explosive with large grain boundaries, and high energy density (>10 eV/nm) CO₂-V in quartz-like 3D network structure without grain boundaries.

Conventional energetic materials consist largely of molecular solids with strong intramolecular covalent bonds and weak intermolecular *van der Waals* bonds. The large disparity between the inter- and intra-molecular distances (*e.g.*, $d_{\text{inter}}/d_{\text{intra}} \sim 2.5\text{-}3.0$) results in the relatively low densities (< 2.0 g/cc) and open structures (nearly 90% empty) of energetic molecular solids. Most energetic materials crystallize into structures of relatively low symmetry that are prone to structural distortions and high chemical sensitivities.

The energetic processes of energetic materials can be described in terms of oxidation-reduction reactions within each molecule but also across the molecular interfaces. They are controlled, therefore, by both intrinsic (such as mass and heat diffusion) and extrinsic (structural defects and chemical impurities) properties. The latter often dominates in conventional explosive composites formulated with nonreactive binders and plasticizers. This results in incomplete burning or deflagration due to the limited diffusion across grain boundaries.

Extended solids made of low *Z* elements in diamond-like 3D-network structures overcome the shortfalls of conventional explosives and constitute a new class of energetic materials. The compact energy storage of these structures is second only to that of nuclear materials. They are often chemically inert and frequently exhibit novel thermal, mechanical and optical properties such as super-hardness, high thermal diffusivity, and wide band-gaps. These extended solids are chemically monolithic explosives containing both oxide (O) and fuel (C, N, H etc.) atoms at the respective bond distances. Thus, they burn more completely and predictably. Furthermore, these materials can be doped with functional 3*d*- and 4*f*- transition metals for advanced electro-optical-magnetic properties and performance controls.

POLYMERIC NITROGEN PHASES

Nitrogen molecule represents the strongest covalent bond known, which makes it extremely stable and chemically inert at ambient conditions. It is also the first molecular system predicted to transform into polymeric cubic gauche form of nitrogen (or *cg-N*), prior to the metallization [1], which has been discovered later in laser-heated DAC experiments above 110

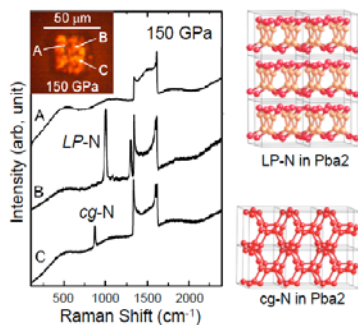


Figure 2. (left) Raman spectra of laser-heated nitrogen at 150 GPa, showing *cg-N*, LP-N and amorphous. (right) Crystal structures of 2D layered LP-N in *Pba2* [4] and 3D network *cg-N* in *I213* [2,3]. Nitrogen remains transparent to 160 GPa- the maximum pressure studied.

GPa and 2000 K [2,3]. This successful prediction of *cg*-N has stimulated the search for other singly bonded polymeric forms of nitrogen and other molecular solids. As a result, a large number (over dozen) of extended nitrogen structures have been predicted to be stable in various forms; yet, the *cg*-N was the only extended phase of nitrogen discovered until very recently. Recently, we discovered new singly bonded extended nitrogen [4], synthesized using laser-heated diamond anvil cells at pressures between 120-180 GPa, well above the stability field of *cg*-N. This new phase was characterized by its singly bonded, layered polymeric (*LP*) structure similar to the predicted *Pba2* [5] and two colossal Raman bands arising from two groups of highly polarized nitrogen atoms in the bulk and surface of the layer, as shown in Figure 2. This finding of *LP*-N, in turn, provided a new constraint for the nitrogen phase diagram, highlighting an unusual symmetry lowering *3D cg*- to *2D LP*-N transition and thereby the enhanced electrostatic contribution to the stabilization of this densely packed layer structure of *LP*-N ($\rho = 4.85 \text{ g/cm}^3$ at 120 GPa).

The discovery of the symmetry lowering transition from *cg*-N to *LP*-N underscores the significance of predicted diamondoid like nitrogen N10 cluster above 200 GPa [6]. The predicted structure of N10 is consisted of even more polarized nitrogen atoms with the sp^2 , sp^3 , and p hybridization. As a result, the bandgap of this materials further opens up to $\sim 4\text{-}5 \text{ eV}$ [5]. Furthermore, the transition from *LP*-N to N10 cluster is expected to accompany further volume collapse by roughly 5% at 250 GPa despite its lower dimensional structure.

POLYMERIC CARBON MONOXIDE PHASES

Carbon monoxide is one of the first molecular systems found to transform into a highly disordered and colored (yellow to dark brown) nonmolecular “polymeric” solid above 5.5 GPa [7]. This polymeric CO (or pCO) is a high-energy density solid [8], as predicted in its isoelectronic system of polymeric nitrogen, *cg*-N.¹ Yet, the crystal structure of pCO and the mechanism of polymerization are not well understood. This is largely due to an unstable nature of pCO; it is highly photosensitive, strongly hygroscopic, and chemically unstable at ambient conditions. Recently, we have studied the phase/chemical transformations of pure CO to 160

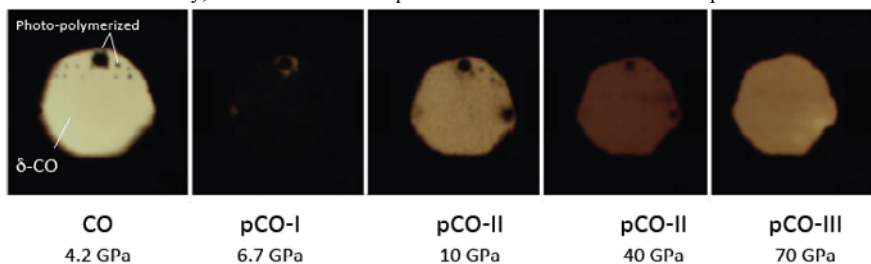


Figure 3 Microphotographic images of CO phases at various pressures, showing a series transformations of molecular CO to opaque polymeric CO phase I (pCO-I) at 6.7 GPa, translucent pCO-II at 10 GPa, then transparent pCO-III above 50 GPa. Note that pCO-II loses its transparency with increasing pressure, suggesting the pressure-induced decrease of the bandgap to $\sim 40\text{-}50 \text{ GPa}$, above which it transforms to highly transparent pCO-III, which remains transparent to 160 GPa- the maximum pressure studied.

GPa and found the presence of three polymeric phases (depicted as pCO-I, II and III), as shown in Figure 3 [9]. The crystal structures of pCO phases, on the other hand, have not been determined, but inferred based on those predicted [10]. This was due to highly disordered structures of pCO phases at high pressures and chemical instabilities of the recovered phases at ambient conditions. The characteristics of these phases are: (i) highly colored relatively low-density phase I in the predicted linear chain structure [10] or other previously suggested 2D conjugated ladder structures [11], (ii) translucent high-density phase II in the 3D network structure, and (iii) transparent phase III in the 2D layer structure that becomes metallic above 150 GPa. The presence of three polymorphs of polymeric CO then reconciles the discrepancies between the previously reported experimental and theoretical densities, structures, and band-gap energies [8,11]. Clearly, the proposed 3D ($P2_12_12_1$) and 2D ($Cmcm$) structures [10] are more consistent with the observed properties of phase II and phase III, respectively. The estimated density 2.4-2.7 g/cm³ of the recovered products from 9-12 GPa [9] agrees well with the calculated one, 2.7 g/cm³ and 3.2 g/cm³ [10]. The predicted band gap ($\Delta E_g \approx 1.9$ eV [11] or 4.4 eV [10]) is also consistent with the observed transparency of phase II.

The above-described transformations in dense carbon monoxide underscore an interesting structure-bond relationship and a stepwise polymerization from C≡O in molecular phase, to highly conjugated, unsaturated C=O in the 1D chain or 2D conjugated ladder (phase I), and to mostly saturated C-O in the 3D network (phase II) and fully saturated 2D lamellar layer structures (phase III). The stepwise polymerization is consistent with the sequence of theoretically predicted transitions [10], as well as the recently discovered 3D cg-N to 2D LP-N transformation [4]. Therefore, these results advocate the pressure-induced ionization as the electrostatic stabilization (or structural packing) energy overcomes the electron delocalization (or chemical bonding) energy at very high density states of both CO and N₂.

The similar layered structure observed in dense CO and N₂ is a *deja-vu* of the similar behavior of these two isoelectronic molecular systems below 5 GPa [12] and, in retrospect, it underscores the difference between CO and N₂ in the intermediate pressure range. The presence of small dipole in CO molecules *collectively* induces a different pathway; that is, the observed stepwise polymerization to a single-bonded layered CO polymer. In contrast, molecular δ -N₂ phase undergoes a series of structural distortions to 110 GPa [13] where it eventually polymerizes to cg-N [2,3] and LP-N [4] at high temperatures. Hence, this comparison notes on the chemistry (or kinetics) aspect of the pressure-induced molecular-to-nonmolecular transition in this intermediate pressure range.

COPOLYMERIC CARBON MONOXIDE AND NITROGEN

CO and N₂ are isoelectronic diatomic systems with similar melting temperatures, phase transitions, and crystal structures at low pressures [12]. However, their chemical behaviors are quite contrast. For example, cubic δ -CO ($Fm\bar{3}m$) chemical transforms into a highly colored polymer above 5 GPa, whereas δ -N₂ (isostructural, $Fm\bar{3}m$) undergoes a series of structural distortions and only polymerizes above 110 GPa and 2000 K into singly bonded cg-N. Therefore, it can be considered that the diverse chemical behavior arises from a small dipole on CO molecules, yet collectively large in solid CO at high pressures – a *conjecture yet been proven*. CO-N₂ mixtures, on the other hand, are highly miscible below 5 GPa, providing a way of tuning the magnitude of collective dipoles and presumably chemical reactivity of the mixture. In fact,

recent theory [14] has shown that in CO-N₂ mixtures CO catalyzes the molecular dissociation of N₂, resulting in *1D* copolymers below 18 GPa and *3D* networks at 52 GPa (Fig. 3). Furthermore, the predicted phases are dynamically stable at ambient pressure, also different from both

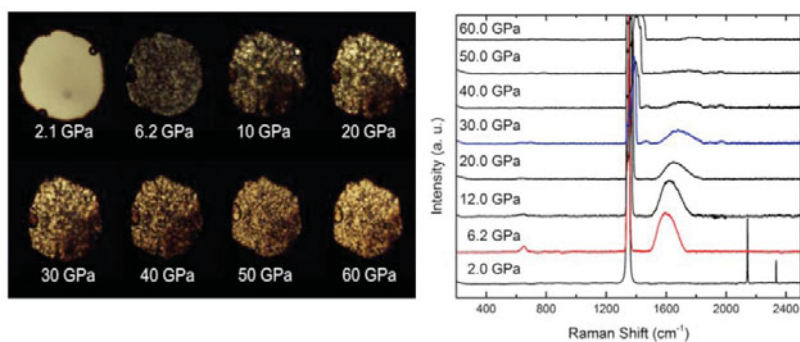


Figure 4 Microphotographic images of 30% nitrogen doped CO (left), showing the pressure-induced polymerization process analogous to those observed in pure and hydrogen-doped CO. Raman spectra of 30% nitrogen doped CO to 60 GPa (right), showing the spectral evidence for the pressure-induced polymerization. At 2.0 GPa, Nitrogen transform from fluid to non-molecular solid phase (β -phase). It is interesting to note that the pure nitrogen solidifies into δ -phase at 4.9 GPa; however, similar to hydrogen doped CO, there was no δ -phase observed in CO-N₂ binary mixture

metastable *poly*-CO and unstable *cg*-N. According to the theory, the predicted copolymers should be recoverable and stable at ambient pressure, providing an opportunity to develop novel high energy density solids. Thus, we propose to investigate chemical reactions between CO and N₂ over a wide range of composition and pressure and, thereby, understand the relationships of chemical reactivity, composition (or dipole), structure, and properties.

Figure 4 summarizes the preliminary results on 3:7 CO:N₂ mixture to 60 GPa showing (a) the pressure-induced visual appearance changes and (b) the pressure-induced Raman spectral changes. These results clearly show visual and spectral evidences for copolymerization of CO and N₂ at pressures as low as 6 GPa. The copolymerization is evident in the Raman spectra from the absence of both CO and N₂ vibron at 6 GPa and the emergence of broad peaks centered around 1600 cm⁻¹ from stretching modes of C/N/O double bonds. The polymerization is also evident from the visual appearance. For example, CO and N₂ mixture forms a transparent, homogeneous mixture at 2 GPa. The mixture remains transparent below 5 GPa; then, it produces “dark” polymer above this pressure. At 6-7 GPa, the entire mixture is converted to the black polymer. Interestingly, this black polymer becomes transparent as pressure increases above 10 GPa, indicating the presence of yet-another polymeric form. The high-transparency of this high-pressure polymer indicates that it is made of single bonded network structure. The absence of 1600 cm⁻¹ above 40 GPa also supports the formation of singly bonded C/N/O polymer. Therefore, the present results indicate a stepwise polymerization occurs in N₂+CO mixture.

CONCLUSIONS

In recent years, a significant number of low Z extended solids consisting of first- and second-row elements well beyond those of CO and N₂ described above have been discovered by the application of high pressure and temperature. These dense covalent or ionic network structures exhibit unusual properties well beyond its high energy density, to novel electro-optical properties such as high second harmonic generation [15], and high superconductivity [16]. However, being synthesized at high pressures, most of these materials transform back to their molecular states upon release of pressure, thus losing their novel properties. Therefore, to utilize these novel extended solids at ambient conditions, future research should emphasize to develop the synthetic pathways to low Z extended solids that are amenable to scale-up synthesis and ambient stabilization. In this regard, the present study on CO-N₂ mixtures can be considered as an alternate synthetic route for nitrogen-rich extended solids using catalytic CO that polymerizes at substantially lower pressures and can be recovered at ambient conditions.

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