Modifying Carbon Nitride through Extreme Phosphorus Substitution

Qianqian Wang,*†∥ Huiyang Gou,†‡ Li Zhu,† Haw-Tyng Huang,* Arani Biswas,* Brian L. Chaloux,* Albert Epshteyn,*∥ James P. Yesinowski,* Zhenxian Liu,* George Cody,† Mengdong Ma, Zhisheng Zhao, Yingwei Fei,† Clemens Prescher,* Eran Greenberg,* Vitali B. Prakapenka,* and Timothy A. Strobel*†∥

*Geophysical Laboratory, Carnegie Institution for Science, Washington, D.C. 20015, United States
†Center for High Pressure Science and Technology Advanced Research, Beijing 100094, China
∥Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, United States
‡Center for Geosciences and Geotechnical Research, Department of Civil and Environmental Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, United States
§Naval Research Laboratory, 4555 Overlook Avenue, SW, Washington, D.C. 20375, United States
¶Institute of Materials Science, Department of Civil and Environmental Engineering, The George Washington University, Washington, D.C. 20052, United States
▽State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China
#Institut für Geologie und Mineralogie, Universität zu Köln, Zülpicher Straße 49b, 50674 Köln, Germany
⊥Center for Advanced Radiations Sources, University of Chicago, Chicago, Illinois 60637, United States

Supporting Information

ABSTRACT: A glassy carbon phosphonitride material with bulk chemical composition roughly approximating C$_3$N$_3$P was synthesized through a high-pressure, high-temperature process using a pure P(CN)$_3$ molecular precursor. The resulting material was characterized using a variety of techniques, including X-ray scattering, pair distribution function analysis, $^{31}$P, $^{13}$C, $^{15}$N magic-angle spinning nuclear magnetic resonance spectroscopy, X-ray photoelectron spectroscopy, and Raman and IR spectroscopies. The measurements indicate that HPHT-C$_3$N$_3$P lacks long-range structural order with a local structure predominantly composed of a sp$^2$, s-triazine-like network in which phosphorus atoms substitute for bridging nitrogen sites found in related C$_3$N$_4$ materials. The HPHT-C$_3$N$_3$P sample exhibits semiconducting properties, with electrical transport dominated by variable-range hopping. The high phosphorus content of HPHT-C$_3$N$_3$P (approaching 13 at. %) is associated with a major decrease in the optical absorption edge ($\sim$0.4 eV) and a $\sim$10$^{10}$-fold increase in electrical conductivity, as compared to previously-reported P-doped graphitic g-C$_3$N$_4$ (0.6-3.8 at. % P). The HPHT-C$_3$N$_3$P sample is considerably harder than layered g-C$_3$N$_4$ and exhibits superior thermal stability up to $\sim$700 °C in air. These results demonstrate a remarkable range of tunable properties possible for C$_3$N$_3$P-related materials through elemental substitution and provide valuable information to guide the design of new materials.

Carbon nitride materials have received considerable interest for decades from both scientific and technological perspectives. Hypothetical three-dimen-

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sional C$_3$N$_4$ frameworks predicted from ab initio calculations are promising candidates for superhard materials because of their strong covalent C–N bonds.\textsuperscript{1–4} Additionally, graphitic C$_3$N$_4$ (g-C$_3$N$_4$) has been investigated as a metal-free, nontoxic semiconductor ($E_g \approx 2.7–2.8$ eV) that demonstrates photocatalytic activity for water splitting and CO$_2$ reduction.\textsuperscript{5–7} However, synthesis routes and materials properties for C$_3$N$_4$-based materials require optimization to realize specific applications including energy conversion and advanced structural performance. For example, light absorption of g-C$_3$N$_4$ is not optimized in the visible region of the spectrum where sunlight has its maximal intensity, and crystalline sp$^3$-bonded 3D C$_3$N$_4$ materials have not yet been definitively synthesized.

Different methods, such as structural amorphization or the intentional introduction of impurities, have been applied to alter and improve the optical, mechanical and electrical properties of C$_3$N$_4$-based materials. Amorphous C$_3$N$_4$ possesses a reduced optical absorption edge (1.90 eV) compared to the crystalline layered counterpart (2.82 eV), leading to superior activity for hydrogen generation in the visible light region.\textsuperscript{8} Phosphorus-doped g-C$_3$N$_4$ (0.6–3.8 at. % P) has been synthesized through chemical methods to tailor the performance of g-C$_3$N$_4$ for photoelectric applications.\textsuperscript{9} The band gap decreases with increasing phosphorus content, as observed via optical absorption spectroscopy and the sample color. The P-doped g-C$_3$N$_4$ samples exhibit increased electrical conductivity and enhanced photocurrent generation, while maintaining the layered structure g-C$_3$N$_4$ based on the presence of crystalline Bragg peaks.\textsuperscript{9–12}

Crystalline phosphorus tricyanide P(CN)$_3$ is an ideal molecular precursor to produce heavily P-substituted C$_3$N$_4$-like materials for study. Chaloux et al. reported an amorphous carbon phosphonitride extended material obtained by thermal self-condensation of molecular P(CN)$_3$ powder sealed under vacuum.\textsuperscript{13} The amorphous structure of this C$_3$N$_4$P material was characterized as a 3D network polymer of disordered, P-bridged s-triazines and s-heptazine-like “phosphohexazines,” that also contains unreacted nitriles. These samples lacked graphic, long-range order, with a measured density of 1.85 g/cm$^3$ and thermal stability to well over 700 °C when heated in air. Recently, a similar material was prepared via solvothermal growth from P(CN)$_3$ in the form of thin films.\textsuperscript{14} A systematic investigation was also previously conducted on the structural and vibrational behavior of molecular P(CN)$_3$ at ambient temperature as a function of pressure. A recoverable C$_3$N$_4$P material resulting from the self-reactions of P(CN)$_3$ above 10 GPa was obtained; however, no characterization of bulk properties was performed.\textsuperscript{15}

In this work, HPHT-C$_3$N$_4$P samples were produced by pressurizing P(CN)$_3$ to 12 GPa and heating at 1000 °C for 30 min using a multianvil press (see Experimental Methods in the Supporting Information). After the high-pressure, high-temperature (HPHT) process, samples were recovered to ambient conditions for characterization. The recovered samples displayed irregular conchoidal fractures and a glassy-carbon-like luster, indicating the production of a nominally amorphous and brittle material. The X-ray scattering patterns of the recovered material show broad peaks indicating the lack of long-range order (Supporting Information). Raman spectra show broad peaks similar to the D and G bands of previously-reported amorphous carbon nitride solids (Supporting Information).\textsuperscript{16} On the basis of comparisons with reports of various amorphous carbons and carbon nitrides, such as a-C$_3$N$_x$\textsuperscript{5,16,17} the X-ray and Raman results indicate that the recovered HPHT material has amorphous character with a large fraction of sp$^2$ bonding. Energy- and wavelength dispersive X-ray spectroscopy (EDS/WDS, Supporting Information) indicate that phosphorus, carbon, and nitrogen appear homogeneously distributed in the sample on the sub-nanometer scale, and yield an average bulk composition of C$_{302.6}$N$_{262.5}$P$_{6.8}$O$_{0.1}$. We suggest that extensive P substitution for N via this molecular pathway helps stabilize this carbon nitride analog, given that other carbon nitrides decompose into graphite and nitrogen under similar temperature and pressure conditions.\textsuperscript{18–21}

Since amorphous materials lack long-range order, structural information is accessible primarily through spectroscopic techniques that probe local bonding and electronic structure. Fourier transform IR (FTIR) spectra of HPHT-C$_3$N$_4$P (Figure S2) indicate the absence of both amine groups (usually present in C$_3$N$_x$-related materials from melamine-containing precursors) and adsorbed water molecules/surface hydroxyl groups. The HPHT-C$_3$N$_4$P sample exhibits several broad IR absorption bands between ~800 and 1600 cm$^{-1}$, which are different from the vibrational frequencies of the P(CN)$_3$ starting material, but similar to C$_3$N$_x$-related materials including amorphous C$_3$N$_4$P$_{1−x}$ and “triazine-based graphic
carbon nitride” (TGCN)\textsuperscript{13,16,22–26} The lower-frequency absorptions are also consistent with phenyl-phosphorus stretching modes as in \(P(C_6H_5)_3\) compounds.\textsuperscript{27} On the basis of the observed vibrational modes, the basic local structure of HPHT-C\textsubscript{3}N\textsubscript{3}P is inferred to be P-bridged heteroatomic C–N rings.

The local structure of HPHT-C\textsubscript{3}N\textsubscript{3}P was further characterized in the bulk and at the surface using magic-angle spinning nuclear magnetic resonance (MAS NMR) and X-ray photoelectron spectroscopy (XPS) (Supporting Information), respectively. The \(^{13}\text{C}\) MAS NMR spectra exhibit a broad peak centered near 125 ppm, indicating the presence of predominantly sp\(^2\) carbon within aromatic or olefinic ring structures (Figure 1a). Compared with other sp\(^2\) carbon materials, such as graphite,\textsuperscript{28,29} triazine/heptazine-based structures,\textsuperscript{30} and graphitic carbon nitrides,\textsuperscript{25} the \(^{13}\text{C}\) spectrum of the HPHT material most closely resembles the related carbon phosphonitride material produced at low pressure.\textsuperscript{13} The HPHT material has a somewhat narrower half-height line width (HHLW) that may indicate it is less disordered, in addition to a small shift to lower frequency compared to the low-pressure phase. Theoretical calculations of the \(^{13}\text{C}\) chemical shifts for a variety of carbon nitride materials\textsuperscript{31,32} are reasonably close to the graphitic carbon nitrides,\textsuperscript{25} the \(^{13}\text{C}\) spectrum of the HPHT material due to greater uniformity, including possibly a more uniform degree of buckling of the graphitic planes when P is the bridging atom. The weak peak at 71 ppm may be due to N atoms bonded to three P atoms, based on the \(^{15}\text{N}\) chemical shift assignment in P\(_2\)N\(_5\) and the \(^{31}\text{P}\) MAS NMR results below.

The \(^{31}\text{P}\) MAS NMR spectrum (Figure 1c) shows several unresolved peaks between −25 and −56 ppm, plus weak spinning sidebands. The lack of significant bulk oxidation in the HPHT sample suggests that these peaks to bridging phosphine (phosphorus) atoms. The absence of a broad peak at +230 ppm assigned to the central P atom in P-substituted heptazine rings,\textsuperscript{13} along with the \(^{15}\text{N}\) results discussed above, suggests that the HPHT sample contains exclusively s-triazine rings. Note also that the \(^{31}\text{P}\) spectrum is similar to P-doped g-C\(_3\)N\(_4\) where P atoms are statistically substituted in “window” and “bay” sites. Because of a longer \(T_1\) value of the low-frequency peak compared to the other peaks in the HPHT material, this peak likely arises from a separate phosphorus nitride phase, the shift being in the region of \(^{31}\text{P}\) shifts observed in P\(_2\)N\(_5\).\textsuperscript{35} This assignment also accords with that made above for the weak \(^{15}\text{N}\) peak.

While bulk HPHT-C\textsubscript{3}N\textsubscript{3}P is disordered and likely contains a broad range of chemical environments, the average local structure appears to best resemble P-bridged s-triazine units on the basis of the above interpretation of FTIR, NMR, and XPS data. We, therefore, constructed an idealized crystalline C\(_3\)N\(_3\)P structure based on TGCN\textsuperscript{35} as a model to compare with experimental MAS NMR and X-ray scattering data. Calculations of the \(^{13}\text{C}\), \(^{15}\text{N}\), and \(^{31}\text{P}\) NMR chemical shifts using this crystalline model, which consists of highly buckled sheets of P-bridged s-triazine, are in good agreement with experimental data (Supporting Information). The experimental pair distribution function \(g(r)\)\textsuperscript{36} obtained from synchrotron X-ray scattering data over a large \(Q\) range, also shows strong similarities with the idealized s-triazine model (Figure 2), providing a convenient framework for interpretation of the local structure.

The first broad \(g(r)\) peak centered at 1.59 Å is attributed to an average distance for C–N/P–C bonds, and lies between the extremes, which are resolved for the idealized crystalline model structure (1.78 Å for P–C and 1.33 Å for C–N).\textsuperscript{37,38} The second \(g(r)\) peak at 2.38 Å represents contributions between second-nearest neighbors within ring environments (C–C, N–N), similar to heterocycles of g-C\(_3\)N\(_4\) as well as pure carbon materials.\textsuperscript{37,39,40} This peak, together with the broad peak centered around 2.9 Å because of intra- and interhexagon distances found in related materials,\textsuperscript{37,40–43} confirms the presence of s-triazine rings in the HPHT-C\(_3\)N\(_3\)P solid.
The temperature dependence of the resistivity under the VRH mechanism is described as $\rho = A \exp(T^{-1/n})$, where $n$ is related to the dimensionality. As shown in Figure 3a, HPHT-C$_3$N$_3$P is described very well when $n = 2$, indicating that Coulomb interactions must be considered, as proposed by Efros and Shklovskii (ES-VRH).

As anticipated from the massive increase in electrical conductivity, the optical absorption edge shifts into the infrared region near 0.4 eV, as deduced from the Tauc plot shown in Figure 3b. Compared with g-C$_3$N$_4$, amorphous C$_3$N$_4$, and P-doped g-C$_3$N$_4$, the extreme P-substitution greatly decreases the absorption edge, making HPHT-C$_3$N$_3$P a narrow band gap semiconductor. The narrow band gap feature extends potential applications of C$_3$N$_4$-based materials into the mid infrared regime and suggests a broad range of materials with tunable optical activity could become available by controlling the level of phosphorus doping.

Previous attempts to produce hard materials from g-C$_3$N$_4$ were unsuccessful due to decomposition under HPHT conditions. The P(CN)$_3$ molecular pathway presented here stabilizes bulk, non-porous ($\rho = 2.87 \pm 0.05$ g/cm$^3$) HPHT-C$_3$N$_3$P material, which allowed for nanoindentation measurements to examine the mechanical properties. Bulk HPHT-C$_3$N$_3$P has an asymptotic hardness of 11 GPa, which is comparable to some carbon nitride thin films, and is more than two times that of glassy carbon. The Young’s modulus of HPHT-C$_3$N$_3$P is $\sim 160$ GPa, which is more than four times that of glassy carbon. In addition, about 50% of the work performed during the indentation is recovered though elastic strain at maximum load (Supporting Information).

In order to examine the thermal stability of HPHT-C$_3$N$_3$P, both differential thermal analysis (DTA) and thermogravimetric analyses (TGA) were performed under inert Ar and 60% O$_2$/40% Ar atmospheres (Figure 3d). In the presence of oxygen, HPHT-C$_3$N$_3$P decomposes at 700 °C with rapid weight loss and exothermic oxidation of the sample. However, when heated under pure Ar, samples maintain >90% of their mass above 850 °C with a broad endothermic peak in the DTA. In contrast, most C$_3$N$_4$ materials decompose well below 700 °C, even under inert conditions.

In summary, an amorphous narrow band gap semiconductor with chemical composition near C$_3$N$_3$P was synthesized in bulk from molecular P(CN)$_3$ at high pressure and temperature. Structural characterization by multiple spectroscopic techniques gives information on the local structure, providing strong indications that s-triazine groups bridged by P atoms form buckled layers, with small domains of a separate phosphorus nitride phase present. The HPHT-C$_3$N$_3$P product possesses superior mechanical properties compared with g-C$_3$N$_4$ and glassy carbon, and exhibits superior thermal stability when compared with g-C$_3$N$_4$, amorphous C$_3$N$_4$, and P-doped layered g-C$_3$N$_4$. Electrical transport of HPHT-C$_3$N$_3$P is dominated by variable range hopping under the Efros–Shklovskii model, and a significantly reduced optical gap and a $10^{10}$ fold increase in electrical conductivity extends potential functionality of C$_3$N$_4$-based materials into the infrared regime. The observed mechanical, optical, electronic and thermal properties for HPHT-C$_3$N$_3$P showcase the exceptional range of tunable properties for C$_3$N$_4$-based materials and provide new directions for synthesis based on novel synthetic pathways and elemental substitution.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmaterialslett.9b00010.

Experimental details, including NMR, XPS, composition measurements, NMR calculation details, FTIR, Raman, X-ray diffraction, and force-indentation curve from nanoindentation measurement (PDF)

AUTHOR INFORMATION

Corresponding Authors
*E-mail: qwang@carnegiescience.edu.
*E-mail: tstrobel@carnegiescience.edu.

ORCID
Haw-Tyng Huang: 0000-0002-9953-1623
Brian L. Chaloux: 0000-0003-0366-2280
Albert Epshteyn: 0000-0002-4489-2296
Timothy A. Strobel: 0000-0003-0338-4380

Present Address
Qianqian Wang, Key Laboratory of Material Physics of Ministry of Education, and School of Physics and Engineering, Zhengzhou University, Zhengzhou 450052, China.

Notes
The authors declare no competing financial interest.

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