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Uniaxial-stress-driven transformation in cold compressed glassy carbon

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We show that transformation of glassy carbon (GC) into a translucent superhard carbon phase by cold-compression is obtained in the presence of a uniaxial stress field. This transition accompanies with sp^2 to sp^3 bonding change in GC, and it is found that the uniaxial stress strongly favors this bonding transition. The transformation of GC causes photoluminescence and significantly increases light transmissivity. Upon decompression, the high pressure phase can be maintained under large uniaxial stress at a chamber pressure even down to ~ 10 GPa. We discuss possible mechanisms of these transitions by a distinct bonding process that occurs in noncrystalline carbon.

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Discovering phase transitions in materials and understanding their mechanisms are very important both from a fundamental perspective and for applications. This is particularly interesting in the investigations of the transformations of carbon materials under extreme conditions such as high pressure because various carbon allotropes with desired properties may be formed which cannot be obtained at ambient conditions thanks to the versatile bonding ability of carbon. The effect of structural order and topology on the evolution between sp^2 and sp^3 bonded carbon structures is a major topic. In fact, all forms of carbon appear to evolve towards the diamond structure^{1–4} under sufficiently high pressure and high temperature (HPHT). The well explored phase diagram of carbon at HPHT is exploited in the commercial production of diamond. Other sp^3 structures, whose nature strongly depends on the topology and degree of order in the carbon precursor, can be stabilized at lower temperatures.^{5–9} For example, graphite transforms into a transparent phase, whose structure is still debated, at above 15 GPa and room temperature.^{10–12} We recently show that carbon nanotubes filled with fullerene C_{70} molecules transform into a quenchable, full sp^3 carbon phase with a monoclinic structure at above 60 GPa.¹³

Compared to the graphitic materials, noncrystalline carbons have recently attracted enormous attention due to their advantages under certain circumstances. Glassy carbon (GC), for example, a highly disordered form of carbon, has been widely used in industry. Different models have been proposed to describe the structure of GC,^{14–16} and the most broadly accepted representation is that it is built up from discrete fragments of curved sp^2 carbon hexagonal sheets in which pentagons and heptagons are found to be intricately distributed.¹⁷ The conditions necessary for the evolution of GC towards a carbon sp^3 hybridized system could be of particular interest when trying to create desired materials and understand the underlying transition mechanism for

amorphous carbon, which is an important topic in materials science which is still far from fully understood.^{18,19}

Glassy carbon transforms into nanocrystalline cubic diamond under HPHT,³ while it transforms into a class of mixed sp^2 - sp^3 compressed GC materials with interesting properties at high pressure and moderate temperature,²⁰ but its transformations under cold compression are more complicated and still debated. The main controversies are as follows: whether there is a pressure-induced bonding change from sp^2 to sp^3 and whether a superhard noncrystalline phase forms in GC (or not) under pressure.^{21–23} Moreover, it is still a challenge to simulate the transitions of GC under pressure in theory because of the lack of long-range translational symmetry in such noncrystalline solids. Therefore, to clarify the transition of GC under pressure and understand the corresponding mechanism is urgent.²⁴ Here, we report the results of a specially designed experiment showing that GC transforms reversibly into a sp^3 -bonded translucent phase. The experiment provides direct evidence that the transition is strongly facilitated when a strong uniaxial stress occurs in the compression conditions. The present results clarify the reasons for the discrepancies between previous works^{21–24} and are also important for the synthesis of noncrystalline superhard carbons with potential applications.

High-pressure Raman spectra of glassy carbon were recorded at room temperature using a spectrometer (Renishaw InVia) equipped with 632.8 nm and 830 nm exciting lasers. Diamonds with 300 μm culets were used as anvils. Stainless steel gaskets, ~ 50 μm in thickness with holes 120 μm in diameter, were used as high-pressure chambers for loading the samples. More details on the experimental setup can be found elsewhere.²⁴ In the high pressure experiments, two or three GC spheres with different diameters (from several micrometers to 40 μm) and a ruby chip for pressure calibration, together with a pressure transmitting medium (PTM), were loaded into the sample chamber. In the experiments, either KBr or liquid N_2 was used as PTM, which gave similar results, indicating that the PTM used is not the dominant factor responsible for the observed transformations in GC

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FIG. 1. (a) Sketch showing the sample loaded into the diamond anvil cell (DAC, left) and the combination of uniaxial stress and chamber pressure exerted on the sphere once it was compressed directly by two anvils (right). (b) Raman spectra from the translucent centres of the big (“B”) and the opaque small (“S”) spheres and from the opaque edge of the big sphere’s (“B-edge”), at 55.2 GPa. Top two spectra were recorded using an excitation wavelength of 830 nm, with bottom four spectra using 632.8 nm. Note that the peak at 1282 cm^{-1} in the top two spectra is not from glassy carbon. The asterisk near 1580 cm^{-1} points to the position of the Raman line for the diamond-GC sphere contact point, which is used to calculate the uniaxial stress applied on GC. The inset shows an optical image of the spheres in DAC taken under back illumination. Liquid nitrogen was used as PTM.

spheres. X-ray diffraction (XRD) measurements were performed at the BL15U1 beamline at the Shanghai Synchrotron Radiation Facility ($\lambda = 0.6199\text{ \AA}$) at room temperature. One-dimensional diffraction patterns were obtained by integrating the two dimensional image with FIT2D software.

As shown in Fig. 1(a), when the large sphere is compressed directly between the two anvils under pressure, stress can be applied to the large GC sphere. This uniaxial stress (P_{ind}) is higher than the quasi-hydrostatic chamber pressure, and the pressure difference increases with increasing pressure as the two anvils approach each other and as the GC sphere itself hardens under deformation. Note that only when the large sphere was pre-compressed to become hard before the bridging and would not break with further compressing, the stress may happen to the sphere in our designed experiments. We found that the uniaxial stress strongly affects the transformation of GC spheres, and at some critical pressure, the center of GC spheres started to turn translucent. These critical pressures differed from experiment to experiment, depending on the magnitude of the stress. Figure 1(b) shows the results obtained at 55.2 GPa from one experiment. In this experiment, the center of the large sphere became translucent above 30 GPa, while the small sphere remains opaque during the compression. The pressure distribution above the translucent center of the sphere is homogeneous and is $\sim 113\text{ GPa}$, as determined from the diamond Raman line because of the direct GC-diamond contact.²⁵ The pressure above the opaque area near the sphere’s periphery and above the small sphere measured by the same method is $\sim 55\text{ GPa}$, which is almost the same as the chamber pressure (P_r) calibrated by ruby. The large differential stress (ΔP) created in the large sphere by the uniaxial force from the two anvils thus caused a significant difference in the transformations of GC between the center and the edge of the large sphere and between the large and the small spheres.

Furthermore, we can show by Raman spectroscopy that there are differences in the bonding characteristics between the translucent and the opaque areas of the large spheres. As we can see from the Raman spectra shown in Fig. 1(b), the G-band of the translucent phase weakens significantly at

such compression conditions and becomes hardly visible. As we know, the G-band of carbon materials is associated with the C-C stretching mode in graphene layers and is a characteristic vibration for sp^2 bonded C.²⁶ The disappearance of this band might indicate that sp^2 carbon structures in the glassy carbon were almost transformed into sp^3 bonded structures. Similar spectroscopic changes have also been observed in the experiment of compressing graphite, in which the G-band broadened significantly when the sp^2 - sp^3 bonding change started and almost disappeared with increasing sp^2 - sp^3 conversion.¹² In contrast, the small sphere shows double bands in the G-band range, which preserves spectroscopic features of glassy carbon. It is interesting to note that the Raman spectra from the opaque part of the large sphere show one broad G-band, located at 1650 cm^{-1} , which are different from glassy carbon but similar to those of graphite/graphitic carbon materials under high pressure, indicating that the microstructures in the GC sphere were changed and graphitic phase might form. This may be due to the shifting

FIG. 2. Raman spectra of GC spheres under different pressure conditions in four separate experiments. The bottom four spectra are all from experiment 4 and were recorded at different pressures during decompression. P_r means the chamber pressure calibrated by ruby, while ΔP represents the difference between P_r and P_{ind} (pressure at the GC-diamond contact area), calculated as $\Delta P = P_{\text{ind}} - P_r$.

FIG. 3. (a) Optical images of three GC spheres at selected pressures in DAC. The last image corresponds to the sample decompressed to 42.7 GPa. The scale bar is 17 μm . All the photos were taken under back illumination. (b) Compression curves obtained by optical imaging in one experiment. We measured the diameter of the GC spheres and then estimated their volumes by the equation $V = \frac{4}{3}\pi r^3$, assuming a spherical shape of the spheres. The compression curve of graphite¹² is added for comparison.

of the graphene layers and responsible for the formation of the transparent phase in GC (see discussion in the last paragraph).

By a series of comparison experiments, we further find that the strength of the uniaxial stress strongly affects the G-band intensities of GC spheres under pressure. Figure 2 shows the Raman spectra collected from several experiments, in which the differences ΔP between the uniaxial stress and the chamber pressure exerted on the GC had different magnitudes. Although the uniaxial stress depends on the sphere size, the chamber pressure, etc., it is clear that a larger ΔP applied on the GC spheres always leads to a lower G-band intensity (Fig. S1 in the [supplementary material](#)), indicating a higher fraction of sp^2 to sp^3 carbon conversion in the compressed spheres. Remarkably, the large uniaxial stress created on the GC spheres and the translucent phase formed can be maintained upon decompression down to at least 17 GPa (experiment 4). In addition, as described in previous work,^{22,24} the yield strength of the superhard GC spheres can be estimated using the calculated ΔP . Here, the very large stress difference ($\Delta P_{\text{max}} \sim 55$ GPa in Fig. 2) sustained by the GC sphere shows that its yield strength is comparable to that of diamond at ambient conditions.

As the densities of carbon materials are critical for their mechanical properties, we thus roughly estimated the volumetric compressions of the compressed GC spheres. Figure 3 shows optical images of GC spheres under pressure from one experiment. From these images, the volumetric compressions of the larger spheres and the small sphere are roughly

calculated to be about 51% and 47% at 53.4 GPa, respectively, by simply analyzing the digital images and assuming an initial spherical shape [Fig. 3(b)]. For comparison, the volume per atom in compressed graphite at ~ 55 GPa decreases to $\sim 59\%$ of the original value.¹² The higher compressibility in glassy carbon should be related to the existence of large amounts of porosity in the material. Furthermore, the deformation of the large spheres due to the direct compression of diamond anvil is significant, while the small one almost preserves the spherical shape and remains opaque during the compression. Thus, the volumetric compression obtained in this way for the large one was underestimated. The initial bulk density of the type I GC used here is $\sim 1.54 \text{ g cm}^{-3}$ and increases to $\sim 3.3 \text{ g/cm}^3$ for the small sphere at 53.4 GPa. The density of the compressed GC is comparable to that of diamond (3.48 g/cm^3). Our X-ray diffraction measurements on the sample confirm that the transformed GC with high density remains noncrystalline (Fig. S2 in the [supplementary material](#)).

We further characterize the optical properties of the translucent GC spheres by optical transmission and photoluminescence (PL) measurements. Figure 4(a) shows the transmission spectra of the large and small spheres at 44.8 GPa after the transition and then upon decompression. It can be seen that the transmissivity of the incident light increases strongly when the GC spheres transform into translucent phases. The absorption band is broad with the center located at 650 nm, and the broadening is consistent with the noncrystallinity of GC. The PL spectra of the two spheres are shown in Fig. 4(b). The PL peak position of both spheres is ~ 660 nm,

FIG. 4. (a) Optical transmission spectra of one big (B) and one small (S) GC sphere at different pressures. Spectra were taken during the decompression process at the pressures indicated. The inset shows an optical picture of the GC spheres in the gasket at 38.3 GPa. (b) Photoluminescence (PL) spectra of the GC spheres at selected pressures.

which is close to that of the absorption peak energy. Moreover, the similar peak positions in PL and transmission spectra of both spheres suggest that the origin of the fluorescence and absorption in the two spheres should be the same, possibly due to the presence of conjugated π -systems (the unconverted sp^2 carbons) distributed in the sp^3 carbon matrix²⁷ of the GC spheres under pressure. Under the same excitation conditions, the PL intensity of the small sphere is obviously higher than that of the big sphere, agreeing well with the fact that more sp^2 carbons were preserved in the small spheres under pressure. Surprisingly, the translucent GC phase can be preserved upon decompression down to ~ 10 GPa (chamber pressure). The optical transmissivity of the sample increases with a slight downshift of the absorption peak energy upon decompression.

Let us now discuss the transition process of glassy carbon into the sp^3 phase in our experiment. Upon compression, when uniaxial stress is absent in the experiment of compressing small GC spheres with diameters less than $10\ \mu\text{m}$, we found that no translucent phase was observed and the Raman spectra of the spheres still exhibited a broad and asymmetric band near 1800 cm^{-1} (similar to the spectra of opaque GC areas shown in Fig. 1) even up to 107 GPa (chamber pressure). In this case, GC spheres are almost isotropically compressed and compacted, probably accompanied by minor sliding and shifting of the contained graphene fragments. From the spatial position point of view, only those sp^2 C atoms which are in appropriate positions, for example, short-ranged ordered carbon sheets distributed in GC, could get converted into sp^3 structures. This process is not sufficient to drive a complete sp^3 carbon conversion in GC. Moreover, the sp^3 structures formed in GC should be harder than the “unbounded” sp^2 structures. Thus, a proper pre-compression could increase the stability of the GC spheres when submitted to large differential stress and favor the later formation of the sp^3 phase. On the other hand, once the uniaxial stress increases on the GC spheres, according to previous literatures,^{28–30} a large pressure difference could generate a significant shear stress/strain. The shear zones should be concentrated in the weaker regions (the unbonded disordered areas), driving atomic displacements. This promotes the sp^2 - sp^3 bonding change in GC and the formation of the sp^3 superhard phase. It can thus be deduced that the sp^3 bonding between C atoms in GC takes place in local areas at the primary compression stage and then spreads to the whole bulk under large uniaxial stress.

In summary, we have demonstrated that the transformation of glassy carbon into a translucent superhard phase is driven by a uniaxial stress field under cold compression. The sp^2 to sp^3 bond conversion in GC is very significant under high stress, causing PL phenomena and a significant increase in light transmissivity. It is important to note that the translucent phase can be preserved even down to around 10 GPa upon decompression by maintaining a large uniaxial stress. The discovery of such an unexpected uniaxial-stress effect on the transformation in glassy carbon will stimulate further studies to search for analogous transitions and understand

the corresponding mechanisms in other noncrystalline solids under compressions.

See [supplementary materials](#) for the analysis on X-ray diffraction data and the curve for the intensities of the “G-band” as a function of pressure difference for Fig. 2.

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