Research article

Super-hard "Tanghulu": cubic BP microwire covered with amorphous SiO$_2$ balls

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A B S T R A C T

Superhard materials, which are widely used in metallurgy, petroleum drilling, and mechanical processing, have become the key to the development of processing and manufacturing industry. Boron phosphide is an excellent Superhard candidate material with excellent inert, high thermostability and heat conductivity. However, since synthesizing BP is a hard task, studies of its basic physical properties and applications are hindered to some extent. Here, we obtained a micron-scale "Tanghulu", in the process of synthesizing boron phosphide single crystals using high-temperature flux method. Under a special appearance, "Tanghulu" is a superhard BP microwire covered by melted or amorphous SiO$_2$ and the hardness of the BP microwires is 40.16GPa. On the basis of a comprehensive material analysis, we established the formation mechanism of this Superhard "Tanghulu" as follows: during the heating process with continuous high temperature, SiO$_2$ molecules on the wall of quartz tube escape and diffuse freely and adhere to the boron phosphide rod-shaped single crystal, which will aggregate then under the effect of surface tension to form an isotropic spherical amorphous SiO$_2$ and form the "Tanghulu" finally. Our work can help to broaden the understanding of micro-scale materials.

1. Introduction

As a Superhard materials, a material with Vickers hardness exceeding 40 GPa is considered [1, 2]. Superhard materials are unique in hardness, incompressible performance, and other aspects unique wear resistance, which are widely used in industrial fields like mechanical processing, oil exploration and geological prospecting, as well as research fields like earth science and high-pressure science [3]. Driven by a rapid growth in manufacturing activity, world's demand for Superhard materials shows a sustained growing tendency. Since the 1950s, there has been a long development stage with the main focus on diamond and cubic boron nitride initially [4, 5]. Unfortunately, both diamond and cBN exhibit some intrinsic defects, such as the poor heat stability of diamond and the low fracture toughness of cBN [6, 7]. Therefore, there was an urgent need to synthesize Superhard materials with improved properties, that is, simultaneously owning high hardness, toughness and thermal stability [3]. In the 1990s, people began to turn their attention to new Superhard materials [6, 8]. After a continuous exploration and reflection, they finally discovered that the light elements, such as B, C, N, and O, and some transition metal elements like Ti, W, and Re, could form compounds with an extremely high hardness [9, 10].

Boron phosphide (BP) is a III-V indirect band gap semiconductor with a band gap of 2.0 eV. It has a zinc blende structure composed of light elements P and B [11]. Similar to diamond and cubic boron nitride, BP has tightly-bound covalent bonds and similar crystal structure, which endows BP with a considerably-high chemical stability that can prevent it from being corroded by concentrated inorganic acids or alkaline aqueous solutions [12]. BP also has excellent thermal stability and can not deteriorate in the air at a temperature of 800–1000 °C [13]. However, if it continues to be heated at a higher temperature (1100 °C), BP will lose phosphorus to form $B_{12}P_2$ [14]. What's more, BP has good mechanical properties. For example, its Vickers hardness can reach 38 GPa [15], which is higher than that of the third-generation semiconductor SiC(22 GPa) [16]; its elastic modulus is as high as 362 GPa; its shear modulus is 157 GPa [17], which is the highest among all binary covalent compounds with sphalerite structure. Besides, BP also has a high thermal conductivity that can reach 460 W/mK[19] according to a latest research. All in all, boron phosphide which combines high thermal conductivity, high hardness and semiconductor characteristics owns a very large research space and great application potential. The excellent stability and heat dissipation capacity make it an ideal semiconductor material for extreme environments and high power conditions. However, research on this
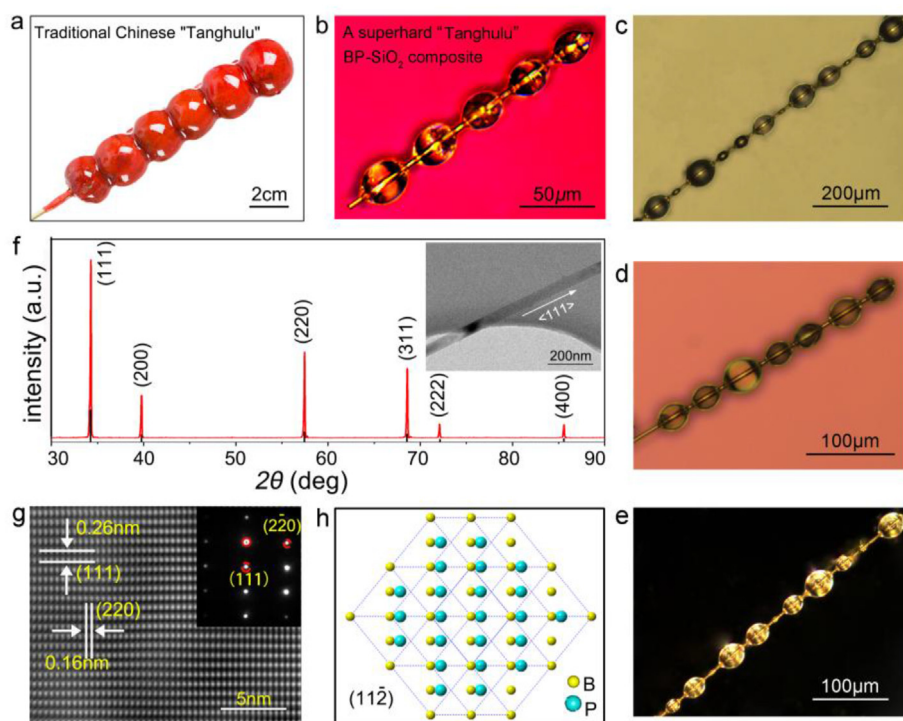

Figure 1. (a) Photograph of traditional Chinese snack "Tanghulu". (b–e) Optical microscope photograph of Superhard "Tanghulu" on different substrates. (f) Powder XRD pattern of experimental BP. Illustration is the TEM image of the main structure BP microrod of "Tanghulu". (g) High-resolution TEM image and diffraction pattern on micro-rod of "Tanghulu". (h) Structural model of BP.
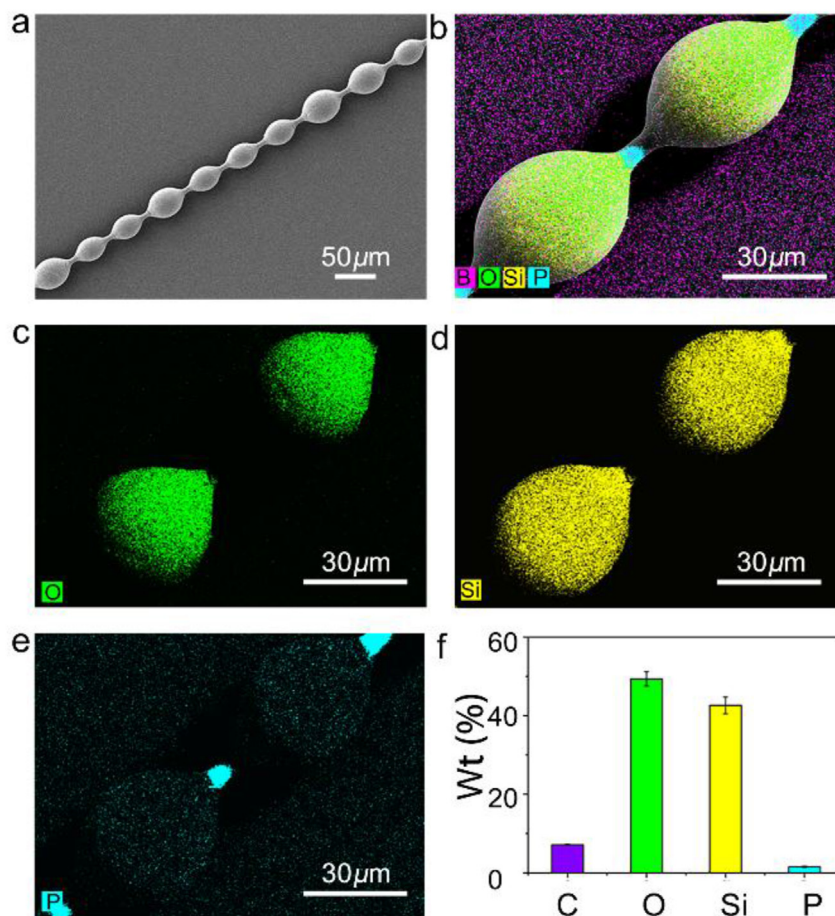

Figure 2. Typical SEM and EDS photographs of "Tanghulu". (a) Low-magnification bright-field SEM image of "Tanghulu". (b), (c), (d), (e) EDS mappings of "Tanghulu" elemental distributions. (f) EDS element quantitative map of "Tanghulu".
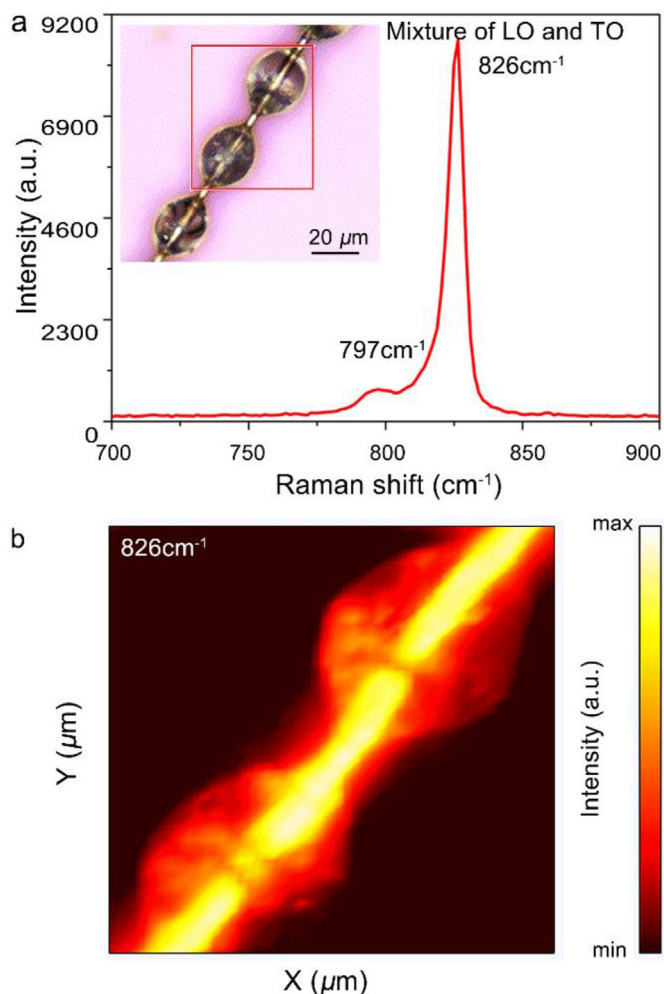
Figure 3. (a) Raman spectrum of the "Tanghulu". (b) Spatially-resolved Raman mapping image of "Tanghulu".

ideal material is hindered by the hard synthesizing process. In this work, we obtained a special micron-scale "Tanghulu" in the process of synthesizing boron phosphide single crystals using the high-temperature flux method, which aroused our interest for a further study. "Tanghulu", as shown in Figure 1a, is a kind of traditional Chinese snack made by stringing hawthorns and other spherical fruits with a bamboo stick and then coating them with maltose syrup. Through X-ray diffractometer (XRD), transmission electron microscope, scanning electron microscope (SEM) combined with energy spectrometer (EDS), Raman spectroscopy

and other characterization methods, it was confirmed that "Tanghulu" is actually a BP microwire covered by melted or amorphous SiO_2. We used a nanoindenter to measure the hardness of BP micro-rod, the body structure of the "Tanghulu", and got the result of 40.16 GPa, which proved it as a Superhard material. Based on the enlightenment of water droplets' gathering on spider silk, we explained the formation mechanism of "Tanghulu" in this work [18]. This study can help expand our understanding of micro-scale materials.

2. Experimental section

2.1. Synthesis of BP containing "Tanghulu"

All reagents and raw materials were purchased from Sigma-Aldrich without any purification. The micron-scale "Tanghulu" was accidently discovered during the process of synthesizing boron phosphide single crystals. First, high-purity amorphous boron powder, red phosphorus, and nickel powder (cosolvent) were weighed according to the chemical reaction measurement ratio (1:1:1.5) and transferred to quartz tube after being ground evenly. Then, we vacuumed the tube till the inside pressure decreased below 10^{-3} Pa and sealed this tube. Secondly, the sealed quartz tube was placed in a tubular furnace, heated to 1150 °C at a heating rate of 5 °C/min, kept it constant for 24 h and stopped being heated when the temperature was cooled to 900 °C at a rate of 2 °C/h. Finally, the sample was cooled to room temperature with the furnace, then washed with aqua regia, deionized water, and ethanol in sequence, and finally dried and collected.

2.2. Characterization

The optical photograph of "Tanghulu" was obtained by a metallurgical microscope (Leica Dmc4500). Powder XRD measurements were performed using X' Pert PRO diffractometer (PANalytical) equipped with X' Celerator RTMS detector and using copper X-ray tube (standard) radiation at 40 kV and 40 mA voltage. The morphology and element distribution of the products were checked by a field emission scanning electron microscope (FESEM) (Zeiss Sigma 300) equipped with an EDS system (XFlash6). The microstructure of main structure micro-rod of "Tanghulu" was revealed by transmission electron microscope (TEM) and the high resolution TEM (HRTEM) images (Titan G260-300). The Raman spectrum was obtained by RENISHAW Ren Cam spectrum equipped with 488 nm laser. The hardness of the BP micro-rod, or the main structure of "Tanghulu", is measured by a nano-indenter (Tl-950, Bruker).

3. Results and discussion

The optical photograph of Superhard "Tanghulu" sample is shown in Figure 1b, c, d, e. Its appearance is very similar to that of traditional
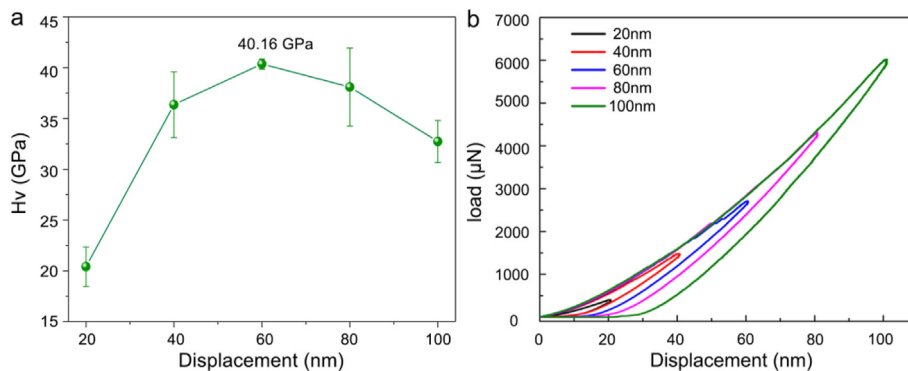

Figure 4. (a) Vickers hardness-indentation depth curve of boron phosphide for the main structure of "Tanghulu". (b) Load-indentation depth displacement curve of the main structure BP microrod of "Tanghulu".
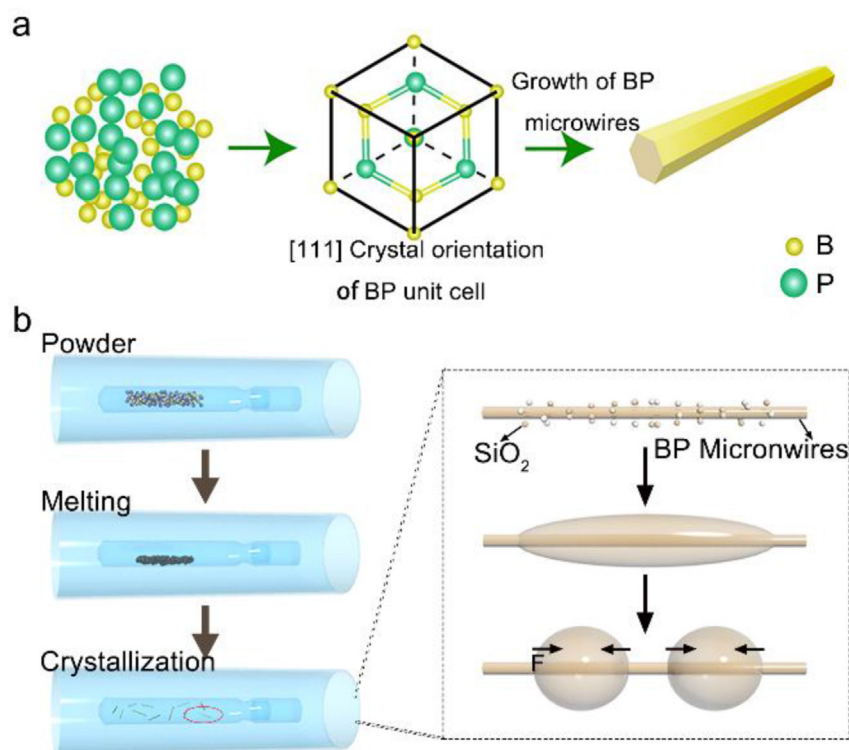
Figure 5. Diagram of the formation mechanism of "Tanghulu". (a) BP microrod growth. (b) Process of growing amorphous SiO_2 balls on the surface of BP microrod.

Chinese snack "Tanghulu". Its length is distributed in the sub-millimeter range. The sphere is transparent, and an internal rod-like structure can be observed through the sphere. Figure 1f shows the XRD spectrum of experimental BP. The diffraction peaks are well recognized as the cubic crystal structure of BP (ICDD no.03-065-0842, space group: F-43m, a = b = c = 4.5430Å, α = β = γ = 90°). As shown in the illustration, TEM image revealed that the micron-rod of "Tanghulu" have smooth surface and uniform diameter, and the growth direction is < 111>, which is consistent with the priority stacking of diamond-like cubic structure [19, 20]. As shown in Figure 1g and the illustration, HRTEM images and selected area electron diffraction (SAED) patterns reveal a further understanding of the microstructure of the micron-rod of "Tanghulu".The lattice fringes with a D-spacing of 0.262 nm and 0.160 nm are observed, corresponding to the (111) and (220) crystal plane distance of cubic BP, respectively. Figure 1h is the crystal structure model of cubic BP, the observation direction is $[11\bar{2}]$.

To obtain the exact composition of "Tanghulu", we used a FESEM equipped with an EDS to characterize the morphology and composition of "Tanghulu". Its SEM image (Figure 2a) shows that its spherical structure has a smooth surface with no impurities attached. According to the EDS image of "Tanghulu" (Figure 2b, c, d, e, f), it is found that the spherical position contains 4 elements Si, O, B, and P, among which oxygen and silicon are evenly distributed and similar in content, while a large amount of phosphorus and a very small amount of boron are distributed in the rod-shaped area. It is worth noting that the background of this EDS mapping image also contains phosphorus and boron, which is because EDS is a device used for quickly analyzing the elements between Bi–U in a micro area. In practical applications, elements with an atomic number less than 8 or with less content are more difficult to be detected accurately. According to the EDS results, we can preliminarily conclude that the spherical position of "Tanghulu" is composed of SiO_2.

The Raman scattering spectrum of "Tanghulu" at room temperature is shown in Figure 3. There are two Raman peaks at 797 cm^{-1} and 826 cm^{-1}, which are respectively referred to as TO and LO phonon vibration modes [21, 22, 23]. Based on the latest report by Zhu et al. [24], we attribute the strongest peak at 826 cm^{-1} to the TO-LO mixed pattern. Based on the work of Zheng et al. [25], In this work, it is considered that the 797 cm^{-1} peak is caused by isotopic disorder, and the scattering involves LO phonons near X or K point [26, 27]. The Raman mapping diagram of "Tanghulu" (Figure 3b) further shows that the main rod structure is a cubic BP and the spherical structure is amorphous SiO_2, and the signal at the spherical position is obtained by amorphous SiO_2 scattering. Accordingly, we can confirm that the synthesized special morphology "Tanghulu" is a composite structure composed of rod-shaped single crystal BP and spherical amorphous SiO_2.

Furthermore, we conducted a nanoindentation measurement with mixed indentation depth on the Vickers hardness of micro-rod, the body structure of "Tanghulu", as shown in Figure 4a. Before the measurement, sample "Tanghulu" was fixed with epoxy resin, and a smooth mirror with random crystal plane orientation was prepared by polishing. Figure 4b is the load-indentation depth displacement curve of nanoindentation. The hardness of sample can be obtained by Oliver-Pharr (O&P) method [28, 29]. Figure 4 displays how the Vickers hardness changes with indentation depth. When the indentation depth is 60nm, the hardness reaches the maximum value of 40.16 GPa, which exceeds the threshold of Superhard material of 40 GPa; when the critical indentation depth is higher than 60 nm, plastic deformation begins to prevail.

Combining our understanding of crystal growth process with an inspiration from the mechanism of water droplet aggregation on spider silk put forward by Zheng *et al.* [18], we inferred the formation mechanism of "Tanghulu".The formation mechanism includes two stages: the growth of cubic BP microrod and the process of its surface enrichment of amorphous SiO_2 balls. **1)** BP microrod growth (Figure 5a): When the temperature is maintained at 1150 °C, the red phosphorus enters a vapor state and the nickel powder enters a molten state. The molten nickel promotes the rapid diffusion of boron in molten state and makes a full contact with the phosphorus vapor. In the slow cooling process, homogeneous boron phosphide crystals are formed, which grow along [111] crystal direction and form the cubic BP single crystal with rod-like structure. During this process, since the temperature is kept above

1000 °C for a long time (about 100 h), partial SiO_2 in the quartz tube wall escapes and exists in the tube as gaseous molecules. **2)** Process of growing amorphous SiO_2 balls on the surface of BP microrod (Figure 5b): the freely diffusing SiO_2 molecules in quartz tube will use rod-shaped BP as the attachment site. Under the force of surface tension, they tend to form droplet-shaped amorphous SiO_2. With reaction time extends, the amorphous SiO_2 balls gradually grow up and finally form a special "Tanghulu" structure, that is, a BP microwire covered by melted or amorphous SiO_2.

4. Conclusion

In this work, we synthesized a composite material with an appearance of "Tanghulu" and a Superhard characteristics. "Candied haws" is actually a composite of BP microwires covered with amorphous SiO_2, and the hardness of the main BP microwires is 40.16GPa. Induced by the accumulation of water droplets on spider silk, we explained the formation mechanism of this "Tanghulu" structure. In addition, the study showed that the process of synthesis of BP single crystal by high temperature flux method using quartz tube as reaction vessel may cause a small amount of SiO_2 to escape and adhere to the surface of BP, thereby limiting the growth of BP crystals. This work has certain reference value for the study of boron phosphide single crystal growth by high-temperature flux method.

Declarations

Author contribution statement

Yali Liang: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Xuefang Lu: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Ying Ding: Analyzed and interpreted the data; Wrote the paper.

Wei Zheng: Conceived and designed the experiments; Wrote the paper.

Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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