A Convenient Low-temperature Route to Nanocrystalline Boron Phosphide

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Nanocrystalline boron phosphide (BP) has been prepared by the reaction of PCl_3 with $NaBH_4$ at 600 °C in an autoclave. The X-ray powder diffraction patterns can be indexed as cubic BP with the lattice constants of $a = 4.53$ Å. The transmission electron microscopy (TEM) image shows particle morphology, with average size of 10 nm for the powders. The selected area electron diffraction (SAED) patterns confirm the prepared BP.

Since the reports of Welker[1] regarding the semiconducting properties of the group III–V compounds, the research on the synthesis of these compounds has attracted interest. Among them, boron phosphide (BP) is a semiconductor with an indirect band gap of 2 eV,[2] which has other superior properties such as high hardness,[3] resistance to chemical corrosion,[4] and high thermoelectric power for direct energy conversion.[5,6] So boron phosphide would be a promising material to be used in modern technology.

Traditionally, boron phosphides were synthesized via various high-temperature reactions (up to 1000 °C).[7] Kumashiro et al. prepared boron phosphide films by photo- and thermal chemical vapor deposition processes.[8] Groshens et al. prepared BP by pyrolysis of phosphinoborane compound precursors.[9,10] However, it is difficult to obtain boron phosphide nanomaterials by these methods. Recently, Schroten et al. synthesized nanometer-scale boron phosphide by vapor–liquid–solid chemical vapor deposition.[11] Our group synthesized ultrafine and nanocrystalline cubic BP by reacting boron powders or BBr_3 with PCl_3 and alkali metals through a solvothermal method.[12,13] However, carbon may come from carbonization of benzene as the reaction is strongly exothermic by above solvothermal method.

Herein, we report a convenient route to nanocrystalline BP by the reaction of PCl_3 and $NaBH_4$ at 600 °C in an autoclave.

The reagents were both analytically pure. All of the manipulations were carried out in a dry glove box filled with N_2. Firstly, 0.03 mol liquid PCl_3 and excessive 0.08 mol $NaBH_4$ powders were placed into a stainless steel autoclave with a quartz-tube liner. And then, the autoclave was sealed and heated at 600 °C for 6 h, followed by naturally cooling to room temperature. The product was washed with distilled water and absolute ethanol for several times to remove the impurities. Dark brown powders were obtained by vacuum-dried at 60 °C for 4 h.

X-ray powder diffraction (XRD) pattern measurement was carried out by a Rigaku Dmax-γA X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å). The morphology of nanocrystalline BP was observed from transmission electron microscopy (TEM) images taken with a Hitachi H-800 transmission electron microscope. X-ray photoelectron spectra (XPS) were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer, using non-monochromatized Mg Kα X rays as the excitation source.

Figure 1 shows the XRD pattern of the product. In Figure 1, all of the four peaks at d spacings of 2.60, 2.28, 1.60, 1.37 Å can be indexed as cubic BP ((111), (200), (220), (311)). The lattice constants are $a = 4.53$ Å, in good agreement with $a = 4.55$ Å (JCPDS card# 75-0394). No evidence of B_2O_3, NaCl, and other impurities is observed. The broadened nature of the peaks indicates that the grain sizes of the sample are on the nanometer scale. The crystallite size is estimated to be about 10 nm in diameter, according to the reflections by the Debye–Scherrer equation.

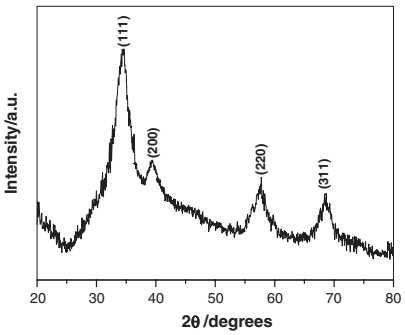

Figure 1. XRD pattern of the as-prepared BP sample.

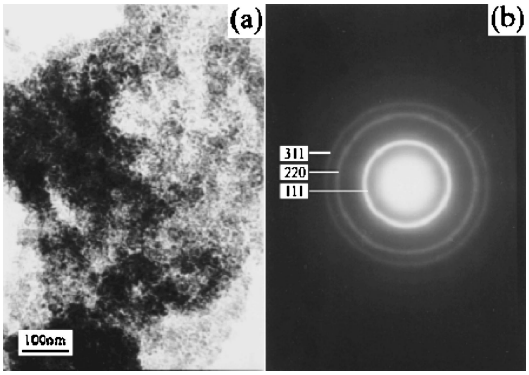

Figure 2. (a) TEM image and (b) SAED pattern of the as-prepared BP sample.

The TEM image and selected area electron diffraction (SAED) pattern are shown in Figure 2. As shown in Figure 2a, the material prepared at 600 °C exhibits small particle morphology. The particle size is estimated in the range of 10 nm in the diameter, which is in agreement with the value calculated by the Debye–Scherrer equation. In Figure 2b, the diffraction rings from inner to outer, at d spacings of 2.60, 1.60, and 1.36 Å, match BP (111), (220), and (311) planes, in good agreement with the XRD results.

Further evidence by the XPS spectrum for the as-prepared

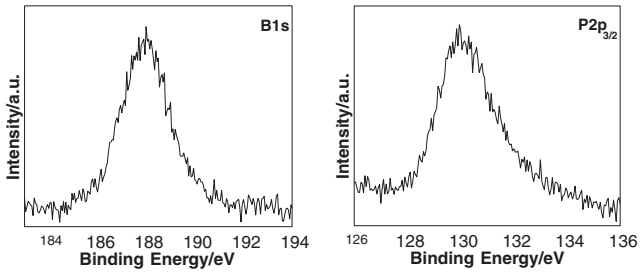

Figure 3. XPS spectra of the as-prepared BP sample.

BP sample is shown in Figure 3. The chemical binding energies of $P2p_{3/2}$ and B1s are located at the positions of 130.1 and 188.1 eV, respectively. The B1s peak at 188.1 eV indicates boron combined with phosphorus forming boron phosphide; this corresponds to the $P2p_{3/2}$ at 130.1 eV, which is considered as the phosphorus bonding with boron forming BP.[14]

The possible formation mechanism of BP was proposed. In the process to nanocrystalline BP by reacting PCl_3 with $NaBH_4$ at 600 °C, the reaction can be described as follows,

$$PCl_3 + NaBH_4 \xrightarrow{600\,^\circ C} BP + NaCl + 2HCl + H_2 \qquad (1)$$

The $NaBH_4$ began to decompose acutely with the temperature increasing (>500 °C)[15] as expressed in Eq 2. The BH_3 reacted further with PCl_3 (bp = 76 °C) to produce BP and HCl, in which HCl immediately reacts with NaH to produce H_2 and NaCl (Eq 3).

$$NaBH_4 \longrightarrow BH_3 + NaH \qquad (2)$$

$$PCl_3 + NaH + BH_3 \longrightarrow BP + NaCl + 2HCl + H_2 \qquad (3)$$

The reaction temperature and time play very important roles on the formation of cubic BP. When the temperature was higher than 550 °C, the crystallinity and the crystallite size both increased. BP was not synthesized when the temperature was lower than 500 °C. The reaction was usually incomplete and the crystallinity was poor when the reaction time was less than 5 h. However, varying the reaction time between 6 and 12 h did not significantly affect the crystallinity or the particle size. The amount of reactant $NaBH_4$ influences the formation of cubic BP. When PCl_3 reacted $NaBH_4$ with a molar ratio of $PCl_3/NaBH_4 = 1/1$ (0.03 mol $NaBH_4$), the yield and the crystallinity of BP were poor. The maximal pressure is about 15 MPa at 600 °C (0.03 mol PCl_3 and 0.08 mol $NaBH_4$), which is estimated according to the amount of hydrogen treating as ideal gases. It is believed that the increasing pressure in the autoclave may be beneficial to the formation of BP.

In summary, nanocrystalline BP with the cubic cell has been successfully prepared by the convenient reaction of PCl_3 with $NaBH_4$ at 600 °C for 6 h. The TEM image revealed the uniform particles with an average size of 10 nm. The selected area electron diffraction (SAED) patterns confirm the prepared BP.

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