

# Microtubes and balls of amorphous phosphorus nitride imide (HPN<sub>2</sub>) prepared by a benzene-thermal method

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Microtubes, hollow balls, solid balls and square frameworks of amorphous phosphorus nitride imide (HPN<sub>2</sub>) were obtained through the reaction of PCl<sub>5</sub> and NaN<sub>3</sub> using benzene as solvent and hydrogen source under mild conditions; as an inorganic polymer, amorphous HPN<sub>2</sub> with these interesting morphologies may be of potential uses in industries.

The discoveries of fullerene and carbon nanotubes as new forms of matter in the nanoscale range have opened a challenging new field in solid state physics, chemistry, and materials science with many possible applications.<sup>1,2</sup> Since then, much attention has been paid to the development of new methods for the preparation of nanotubes and fullerene-like structures of other materials.<sup>3,4</sup> Besides crystalline nanotubes and fullerene-like structures, amorphous microtubes of molybdenum polysulfide have recently been reported, which undoubtedly indicate that amorphous materials can also aggregate into tube- and ball-like morphologies.<sup>5</sup>

As an inorganic polymer, phosphorus nitride imide (HPN<sub>2</sub>) is one of the ternary phosphorus nitrides. It has been researched for many years,<sup>6</sup> and has a network structure consisting of PN<sub>4</sub> tetrahedra linked through all four vertices by corner sharing; it has isometric analogues in the silicate family.<sup>7,8</sup> Recently, amorphous phosphorus nitride (P<sub>3</sub>N<sub>5</sub>) was synthesized in our laboratory by a solvent-free reaction between PCl<sub>5</sub> and NaN<sub>3</sub> in an autoclave.<sup>9</sup> However, when the reaction was carried out in benzene, amorphous HPN<sub>2</sub> was formed instead of P<sub>3</sub>N<sub>5</sub>. It was also found that microtubes, balls (hollow and solid) and square frameworks of the amorphous HPN<sub>2</sub> could be formed under different reaction conditions. The results are presented here.

The preparation technique was as follows. Manipulations were carried out in a dry glovebox with N<sub>2</sub> gas flowing. Analytically pure PCl<sub>5</sub> (0.005 mol) and NaN<sub>3</sub> (0.025 mol) were put into four stainless steel autoclaves of 25 ml capacity. These were filled with benzene to within 90% of the total volume. Two autoclaves were maintained at 190 °C for 3 d and 10 d, the other two were kept at 250 °C for 12 h and 3 d, respectively. When the heating was over, the autoclaves were allowed to cool to room temperature naturally. The precipitates were collected, washed with carbon disulfide, benzene, absolute ethanol and distilled water several times and dried under vacuum at 80 °C for 4 h.

Elemental† and chemical analyses show that the H:N:P:C ratio in the samples is *ca.* 1:2.02:0.99:0.02. XPS‡ showed that the binding energies of P 2p and N 1s were 133.3 and 398.7 eV, which are close to the values of P<sub>3</sub>N<sub>5</sub>.<sup>10–12</sup> The quantification of peaks confirmed that the atomic ratio of P:N was nearly 1:2.01. No other element except a trace amount of chlorine was detected in the samples. Fig. 1 shows the infrared spectrum§ of the sample, which is in good agreement with the reported spectrum of HPN<sub>2</sub>.<sup>7</sup> Taking the above results into consideration, it is believed that the products are phosphorus nitride imide, HPN<sub>2</sub>.

TEM¶ images of the samples prepared under different conditions are shown in Fig. 2. Microtubes [Fig. 2(a), (b)] were found to exist in the samples prepared at 250 °C for 12 h and

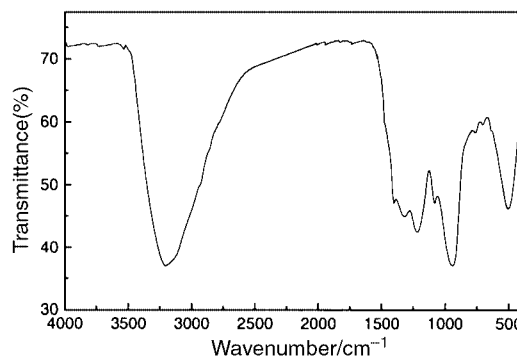


Fig. 1 IR spectrum of the amorphous HPN<sub>2</sub>.

190 °C for 3 d. The proportion of microtubes in the samples was 20–25%. It is evident that the boundary of the wall of the tubes is quite well defined. The external diameter of the tubes is 350–450 nm and the thickness of the walls is *ca.* 100 nm. However, the samples prepared at 250 °C for 3 d and 190 °C for 10 d consisted of hollow balls (15–20%), solid balls (60–70%) and square frameworks (1–2%) [Fig. 2(c), (d) and (e)], respectively. The balls are perispherical with a diameter of 200–300 nm. The thickness of the shell of the hollow balls is *ca.* 50 nm. The frameworks are a uniform square and the length is about 500 nm. Electron diffraction did not reveal any crystal ordering in the tubes, balls and frameworks, and they may be considered as completely amorphous. The result was consistent with the XRD patterns of the samples.

It is believed that the hydrogen element in HPN<sub>2</sub> originated from benzene because P<sub>3</sub>N<sub>5</sub> instead of HPN<sub>2</sub> was produced when the reaction was carried out in a solvent-free environ-

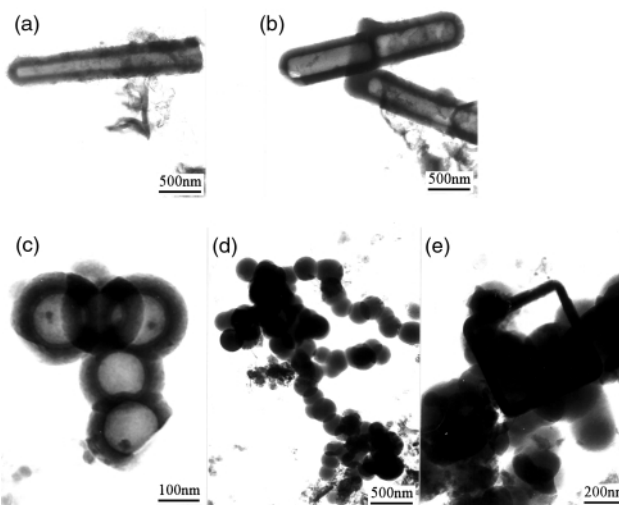


Fig. 2 TEM images of the amorphous HPN<sub>2</sub> prepared (a) at 250 °C for 12 h, (b) at 190 °C for 3 d, and (c–e) at 250 °C for 3 d or 190 °C for 10 d.

ment.<sup>9</sup> Benzene plays an important role in the reaction: it acts not only as a solvent but also as a hydrogen element source, and may be the key to the formation of the interesting morphologies. This process is a complicated reaction and the exact mechanism needs further research. It was found that sodium chloride was the by-product, which was determined by the XRD patterns of the samples not washed with water.

The influence of temperature and time on the synthesis of amorphous HPN<sub>2</sub> was also studied. If the reaction temperature is lower than 190 °C the reaction is very incomplete and only a small amount of HPN<sub>2</sub> can be obtained. But when the reaction temperature is above 300 °C, P–H adsorption at 2080 cm<sup>-1</sup> is detected through IR spectra, indicating that PN<sub>4</sub> tetrahedra are destroyed.<sup>10</sup> For the sample prepared at 190 °C for 12 h, no special morphology was found. The samples prepared at 190 °C for 3 d and 10 d have the same morphologies as those prepared at 250 °C for 12 h and 3 d, respectively, which indicates that a long reaction time and low temperature have the same effect as a short reaction time and high temperature, in the appropriate temperature range. Considering the facts that balls are formed instead of tubes with lengthened reaction time, and that some tubes are found truncated at the middle part [Fig. 2(b)], it is proposed that the hollow balls are transformed from the tubes. Solid balls might be formed through the aggregation of amorphous fragments, which is consistent with the fact that the ball was the most stable state in liquid.

In the reaction temperature range, nothing dangerous took place in our experiments, which indicated that this process was safe even though PCl<sub>5</sub> and NaN<sub>3</sub> were used. As an inorganic polymer, phosphorus nitride imide, HPN<sub>2</sub>, with the above

interesting morphologies may have some potential uses in industry.

## Notes and references

† Elemental analyses were taken on a 240C elemental analysis instrument.

‡ XPS were recorded on an ESCALAB MKII instrument with Mg K $\alpha$  radiation as the exciting source.

§ IR spectra were obtained on a Magna IR-750FT spectrometer.

¶ TEM measurements were made on a Hitachi H-800 transmission electron microscope with an accelerating voltage of 200 kV.

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