Reply to “Comments on the ‘Synthesis of Cubic Boron Nitride at Low-Temperature and Low-Pressure Conditions’ ”

On behalf of all the authors, we wish to express our thanks to Dr. Sachdev for his thoughtful comments on our paper “Synthesis of Cubic Boron Nitride at Low-Temperature and Low-Pressure Conditions” (Hao et al. *Chem. Mater.* **2001**, *13* (8), 2457−2459). We have found Dr. Sachdev’s comments very informative (referred to as “comment” in this article) and acknowledge some deficiencies in our above-mentioned paper (referred to as “paper” in this article). But we take issue with several of Dr. Sachdev’s points, a detailed reply to which follows.

1. Interpretation of XRD Patterns

Dr. Sachdev provided detailed information about the intensity and positions of the XRD peaks of hBN, cBN, and oBN in his comment and pointed out the difference between the crystallographic data and the measurement results in our paper. We observe that the main difference is in the relative intensities of the peaks.

Here, we must point out that the XRD patterns in the paper were obtained on the as-prepared samples, without grinding. Because the growth habit of the crystals was unpredictable, some textures may exist and they will affect the intensities of the peaks.

It is well-known that, in nanocrystals, the density of defects is very high and complicated strains exist.[1] This phenomenon will result in changes of the intensities of the peaks to a rather large extent, and sometimes even their positions also shift. In some kinds of nanocrystals, the intensity of XRD peaks can change significantly.[2]

We acknowledge that we have wrongly identified the peak at about $2\theta = 63.5°$ as the (102) reflection of hBN, whereas it should be indexed as the (214) reflection of oBN. Also, the card (see ref 11 of our original paper) should be 25-1033, not 25-1032.

As has been pointed out in our paper, all the peaks except those of cBN and hBN can be indexed to oBN. The peaks with d values of 0.4777, 0.3520, 0.2491, 0.2060, and 0.2014 nm can be indexed as the (110), (120), (311), (410), (032), and (240) of oBN. We also note that the strongest peak of oBN cannot be observed in the XRD pattern, the main reason being the existence of texture in the nanocrystals due to the change of growth habit.

2. Interpretation of the IR Spectra

In our opinion, Dr. Sachdev has misunderstood the meaning of ref 14 of our paper. While in this reference it is stated that the IR absorption peak of cBN should be located *at 1050 cm^{-1} or at about 1065 cm^{-1}*, different authors give different values for the IR peak of cBN.

The positions of the IR peaks of hBN and cBN can significantly shift with the variation of state and environment of the BN samples. For example, the IR peaks of hBN films can be found in the range of 1400 and 800 cm^{-1} and that of cBN film between 1090 and 1100 cm^{-1}.[3−6] Some authors also report that the position of the IR peaks of hBN and cBN will change with the strain in the film.[5] Another reason for the shift of the IR peak of cBN may be that the peak at 1134 cm^{-1} is a sum of contributions from both cBN and oBN. Thus, we reach the following conclusion: the positions of the IR peaks of both hBN and cBN may shift very much, especially when the samples are in complicated environments.

It is true that both the B−O and B−OH bonds give IR spectra similar to those of BN. In our paper, the peak at 3428 cm^{-1} has been indexed to the B−OH bond formed on the surface of BN nanocrystals. Assuming that Dr. Sachdev is correct, that is, the sample is nothing but boron hydroxide or boron oxide, it is very difficult to explain the fact that no signal of boron hydroxide or boron oxide can be detected by XPS, XRD, and selective area electron diffraction (SAED) measurements.

Due to the fact that we have checked carefully all alternative interpretations, we have drawn the conclusion that BN has been prepared by the benzene-thermal method.

3. Interpretation of the TEM Results

At the beginning of the Results and Discussion section, we gave detailed crystallographic data for cBN. The analysis of the SAED pattern was carried out according to the standard method. Many of the diffraction rings in the SAED pattern can be indexed to cBN, namely, from the inner to the outer: the first, second, and third rings can be indexed as the (111), (220), and (311) reflections of cBN, respectively.

4. About the Experimental Section

From Dr. Sachdev’s comment, we cannot know the method he used to synthesize BN. While it may be true that in his hands only amorphous BN at 500 °C can be obtained, it does not follow necessarily that all BN samples synthesized at 500 °C must be amorphous.

We have truly observed the partial decomposition of benzene at 480 °C, but this phenomenon did not entirely prohibit the crystallization of the BN nanocrystals. Also, we admit that our method has many disadvantages, and the experimental conditions need to be optimized. Just as stated in the background materials we supplied to

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10.1021/cm0220089 CCC: $22.00

Dr. Cora Linda, the author of the paper in *MRS Bull.* (**2001**, Sept, 662), we believe that nearly pure cBN can be synthesized using the same method reported in our paper, by controlling the relative stability of different BN phases.

5. About the Summary and Conclusions

In his comment, Dr. Sachdev mentioned that copper, nickel, cobalt and Fe_2N etc all have similar XRD patterns with that of BN, and their particles could be seen in the TEM photos. Nonetheless, these materials were not detected by IR and XPS.

6. Our Conclusions

We believe that in the preceding reply we have refuted or cast doubt on the major criticisms leveled by Dr. Sachdev in his comment.

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Received June 3, 2002

CM0220089