

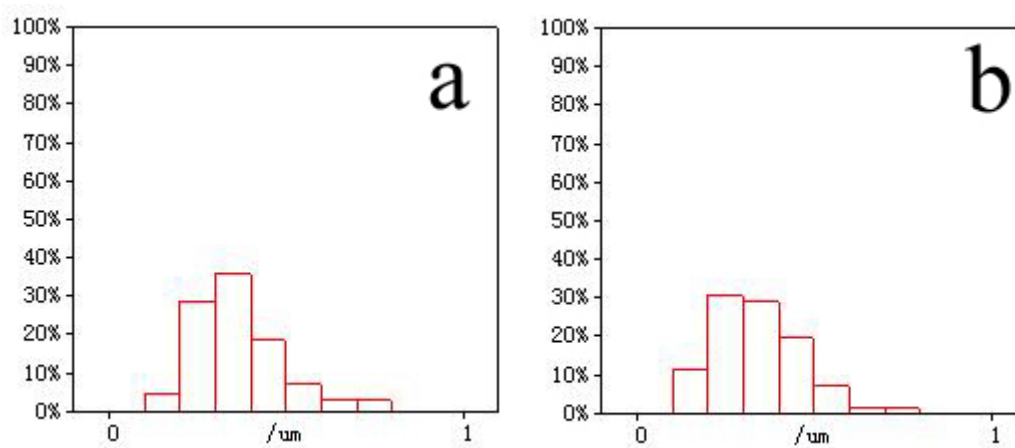
## Supporting Information Available

### Thermal-induced shape evolution from uniform triangular to hexagonal r-BN nanoplates

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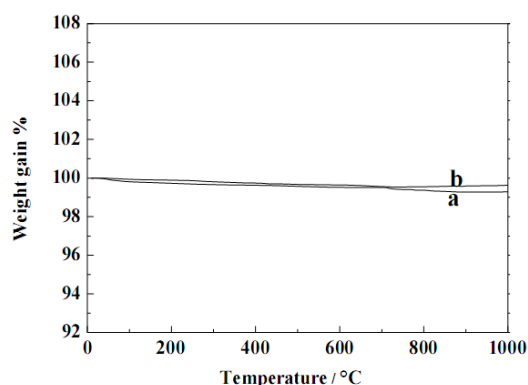
The contents of supporting information include the influences of reaction temperature, ratio of reactants and different reaction systems on the final formation of triangular r-BN nanoplates and the thermal stability of the as-obtained r-BN under nitrogen atmosphere.

**SI 1.** The size distribution histograms of triangular r-BN nanoplates and hexagonal r-BN nanoplates.



**Fig. SI 1.** The size distribution histograms of the products: (a) Sample 1, (b) Sample 2.

**SI 2.** Thermal stability of the as-obtained r-BN under nitrogen atmosphere.



**Fig. SI 2.** The TGA curves of the samples under flowing N<sub>2</sub>: (a) Sample 1, (b) Sample 2.

The thermal stability of the samples (they were dried in a vacuum at 100 °C for 4 h in advance and were rapidly prepared before the detection) were studied by TGA (Fig. SI 2). Fig. SI 2a shows a typical TGA curve of Sample 1, which indicates that their weight remain almost unchanged below 700 °C in floating N<sub>2</sub>. The slightly weight decrease was observed around 700-1000 °C, which might be attributed to the breakup of N-H bonds and appearance of atom vacancies. However, from the TGA curve of Sample 2, we can see that its weight has not changed significantly below 1000 °C, indicating that Sample 2 have a relative higher thermal stability than that of Sample 1 in N<sub>2</sub> atmosphere.

**Table SI 1.** Different proportions of triangular r-BN nanoplates obtained via changing the reaction temperature (Group 1), dosage of the NaNH<sub>2</sub> (Group 2), different boron sources (Group 3), or different nitrogen sources (Group 4).

Group number	NaBH <sub>4</sub> (mol)	NaNH <sub>2</sub> (mol)	T (°C)	t (h)	The proportion of regular triangular r-BN nanoplates
1	1.0	1.5	300	24	none
	1.0	1.5	400	24	none
	1.0	1.5	450	24	~10%
	1.0	1.5	550	24	~90%
	1.0	1.5	600	24	~90%
2	1.0	0.5	550	24	none
	1.0	1.0	550	24	~50%
	1.0	1.5	550	24	~90%
	1.0	2.0	550	24	~90%
3	KBH <sub>4</sub> (1.0 mol)	1.5	550	24	~70%
	KBF <sub>4</sub> (1.0 mol)	1.5	550	24	~60%
	H <sub>3</sub> BO <sub>3</sub> (1.0 mol)	1.5	550	24	~60%
	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> (1.0 mol)	1.5	550	24	~10%
4	1.0	NaN <sub>3</sub> (1.5 mol)	550	24	none
	1.0	NH <sub>4</sub> Cl (1.5 mol)	550	24	none
	1.0	CO(NH <sub>2</sub> ) <sub>2</sub> (1.5 mol)	550	24	none
	1.0	NH <sub>4</sub> HCO <sub>3</sub> (1.5 mol)	550	24	none

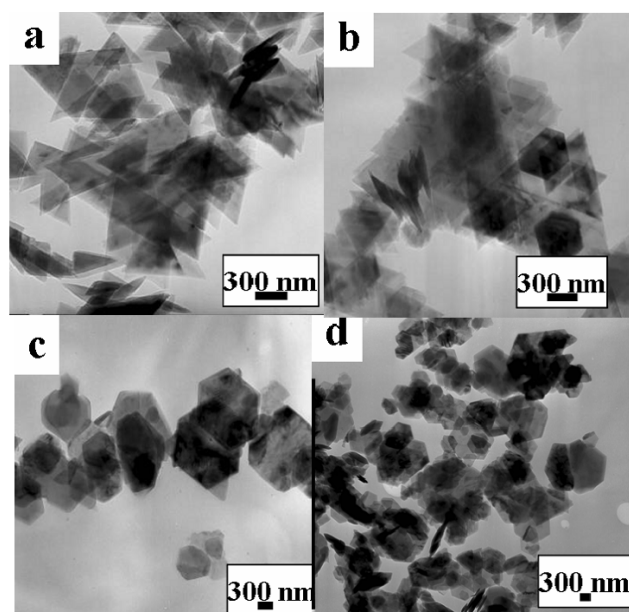
To study the influences of reaction temperature, ratio of reactants and different reaction systems on the final formation of triangular r-BN nanoplates, a series of contrast experiments were further carried out (listed in **Table SI 1**), it is found that boron nitride could not be obtained below 400 °C. If the reaction temperature was further raised to 450 °C, boron nitride with mixed phases (JCPDS card nos. 34-0421 and 45-1171) were produced and the proportion of triangular nanoplates was small (~10%). If the temperature was further raised, such as at 550, 600, or 650 °C, boron

nitride with pure rhombohedral phase (JCPDS card no. 45-1171) were obtained, and the proportion of uniform triangular r-BN nanoplates was dramatically increased to ca. ~ 90% of the whole product. However, the higher reaction temperature (above 650 °C) usually leads to the lower yield (or the higher agglomeration degree) of triangular r-BN nanoplates. The experimental result shows that the lowest reaction temperature for the synthesis of the highest proportion of triangular r-BN nanoplates was at 550 °C. The dosage of the NaNH<sub>2</sub> can affect the proportion (Group 2), it is obvious that the relative high content of NaNH<sub>2</sub> was preferable for the fabrication of triangular nanoplates. When the dosage of NaNH<sub>2</sub> was in excessive, NaBH<sub>4</sub> was substituted by other boron sources (such as KBH<sub>4</sub>, KBF<sub>4</sub>, H<sub>3</sub>BO<sub>3</sub>, or Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>), triangular r-BN nanoplates could also be obtained. However, when NaNH<sub>2</sub> was substituted by NaN<sub>3</sub>, NH<sub>4</sub>Cl, CO(NH<sub>2</sub>)<sub>2</sub>, or NH<sub>4</sub>HCO<sub>3</sub>, no triangular r-BN nanoplates were observed.

**Table SI 2** Morphology of the final products at different calcination temperature (Group 1) and time (Group 2).

Group number	Calcination temperature (°C)	Calcination time (h)	Morphology of the final product
1	600	8	triangular r-BN nanoplates (~90%).
	800	8	irregular shaped triangular r-BN nanoplates.
	1000	8	hexagonal r-BN nanoplates (~70%).
	1200	8	most are irregular shaped plates.
2	1000	4	triangular r-BN nanoplates.
	1000	6	most triangular r-BN nanoplates were truncated.
	1000	8	hexagonal r-BN nanoplates were obtained with the highest proportion (~70%).
	1000	10	irregular hexagonal r-BN nanoplates.

**SI 3** The shapes of the products obtained under different calcination temperatures.



**Fig. SI 3.** The shapes of products obtained under different calcination temperature for 8 h. (a) 600 °C, (b) 800 °C, (c) 1000 °C, (d) 1200 °C.

The effects of the calcination temperature on the final morphology of the products were also investigated (Fig. SI 3), it is found that the calcination temperature plays an vital role in the morphology conversion. The shape of the triangular nanoplates were almost unchanged under 600 °C (Fig. SI 3a), however, when the calcination temperature was elevated to 800 °C, irregular triangular nanoplates and tiny hexagonal nanoplates were coexisted (Fig. SI 3b), once the sample was calcined at 1000 °C for 8 h, uniform hexagonal nanoplates were obtained (Fig. SI 3c). Whereas, if

the calcination temperature was increased to 1200 °C, the hexagonal nanoplates began to crash (Fig. SI 3d). Therefore, the optimal calcination temperature for the formation of regular hexagonal nanoplates was 1000 °C.

SI 4 The FTIR spectra of Sample 1 and 2 dried in a vacuum at 60 °C for 12 h.

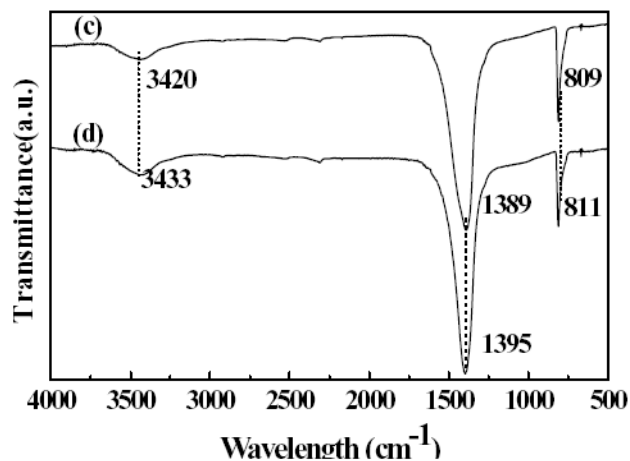


Fig. SI 4 The FTIR spectra of Sample 1 and 2 dried in a vacuum at 60 °C for 12 h.