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Synthesis of polymorphic titanium oxide nanoparticles by a rapid gas-phase chemical reaction

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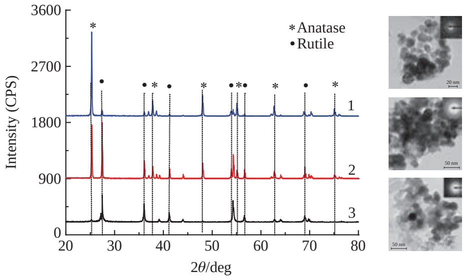
A gas phase reaction was proposed for the production of high dispersity polymorphic titanium oxide (TiO_2) nanoparticles in a closed detonation device. The phase structure, morphology and composition of TiO_2 were characterized by XRD, TEM and EDX analysis.



Titanium oxide crystallizes in several crystallographic polymorph phases, the most popular of which are anatase and rutile. Anatase is mostly formed at low temperatures, while rutile is thermodynamically stable at higher temperatures. Owing to its outstanding properties, polymorphic nanostructured TiO_2 has comprehensive applications in pigment, sunscreens, ceramics, cosmetics, biomedicines, electronics, environmental remediation, photocatalysts, solar energy cells, gas sensors,[1–10] *etc*. Various routes for the preparation of TiO_2 nanoparticles have been reported, including solution-phase synthesis, solid-phase synthesis, gas-phase synthesis, *etc*. On the basis of previous research,[11–13] we report that the sphere, high dispersity rutile, anatase and their mixture phase TiO_2 can be easily obtained through adjusting the gas-phase precursor composition and reaction conditions and characterize its structure, morphology and composition in this work.

A controllable filling gas (volume ratio, H_2:O_2 = 4:1~2:18) was firstly premixed in a shock tube (length, 2200 mm; circular tube, 80 mm) after evacuation and heated up to 100–150 °C. Then, 0.1 mol of $TiCl_4$ was dissolved in absolute ethanol (0.3–0.6 mol) to form a transparent solution. The solution was atomized in the shock tube and gasified.[†] The sphere, polymorphic TiO_2 nanoparticles were synthesized separately by a rapid gas-phase reaction followed by high-energy igniter with 40 J. The products were characterized by XRD, TEM and EDX analysis.[‡]

As shown in Figure 1, the diffraction peaks of samples 1 and 3 can be indexed to the anatase and rutile phases of TiO_2 (JCPDS nos. 21-1272 and 21-1276). No characteristic peaks of other impurities were detected in the XRD patterns, indicating that the two as-obtained TiO_2 products have good crystallinity. It is clear that the sphere anatase TiO_2 has an average particle size of about 14 nm and rutile TiO_2 has an average particle size of about 28 nm. Moreover, the XRD pattern of sample 2 suggests that it is composed of a mixed TiO_2 phase, mainly including rutile and anatase; the peak of brookite does not appear. It is well known that if a sample contains anatase and rutile crystal forms, the mass fraction of rutile (W_R) can be calculated as $W_R = A_R/(0.884A_A + A_R)$, where A_A and A_R are the integrated intensities of the anatase (101) and rutile (110) peaks. Table 1 summarizes the structure and morphology of the products. When going from sample 1 to sample 3, the diffraction peak of anatase becomes weaker; however, the diffraction peak of rutile is increasingly stronger and sharper with increasing the value of oxygen to mixed

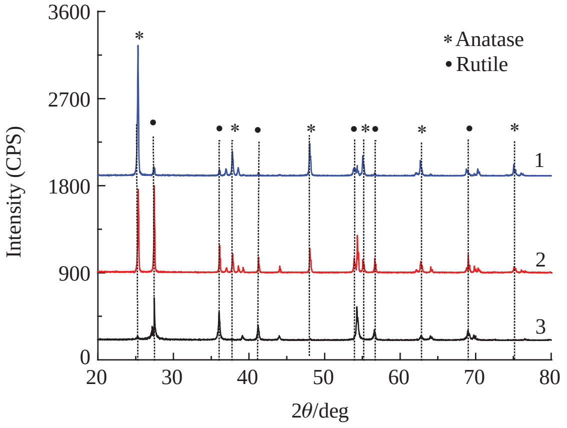


Figure 1 XRD patterns of TiO_2 powders.

[†] The gas-phase experimental equipment was described elsewhere.[11] The chemicals of analytical grade from Nanjing Chemical Reagent Corporation and high-purity gases from Jiangsu Specialty Gases Corporation were used without further purification.

[‡] The XRD analysis was performed on a Rigaku D/MAX 2400 instrument operated at a step size of 0.02° in a range of 20–80° with CuKα radiation (k = 0.15406 nm; voltage, 40 kV; current, 30 mA). TEM analysis was carried out using a TECNAI F-30 microscope (operated at 300 kV, 0.205 nm point resolution and 0.102 nm line resolution) equipped with energy dispersive X-ray spectrometer (EDX).

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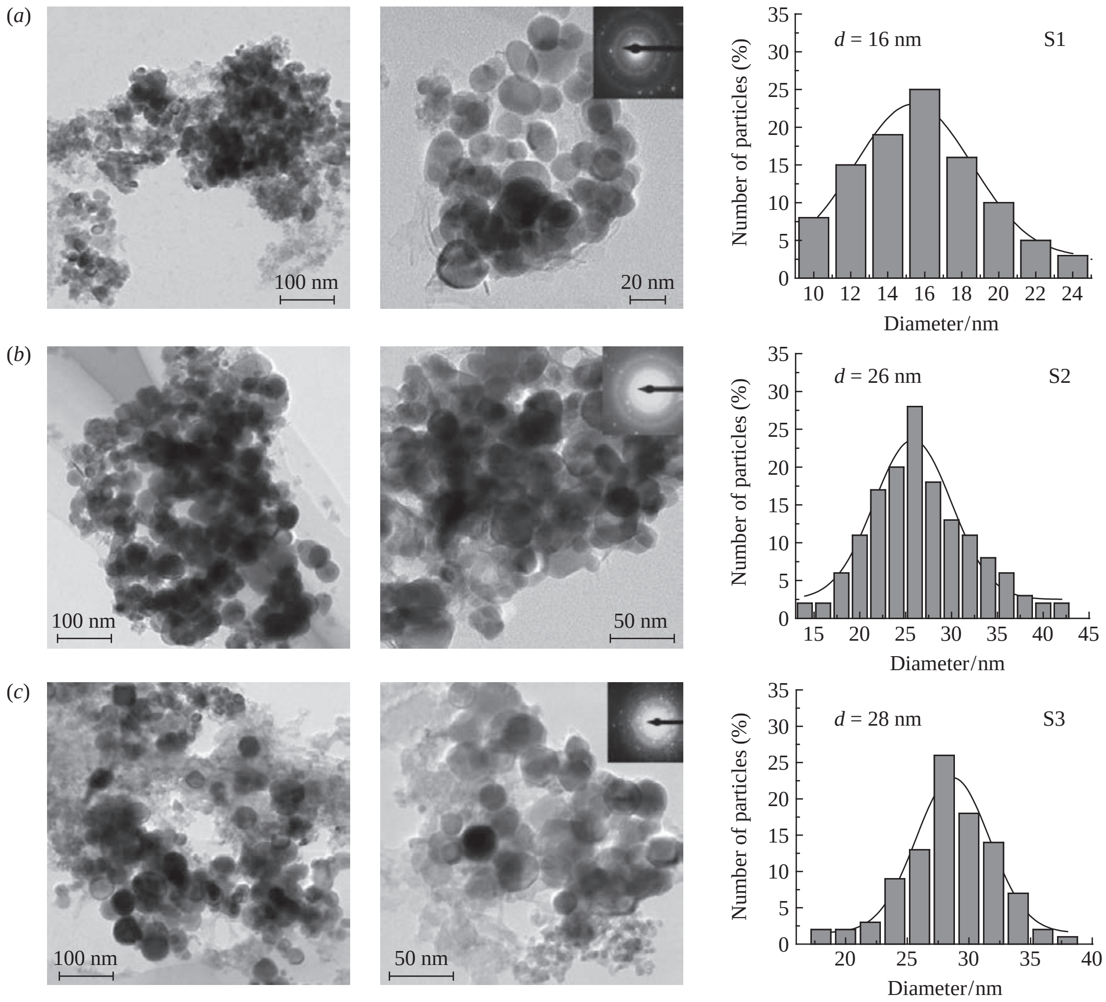

Figure 2 TEM and EDX images of nanoscale TiO_2 and the distribution of particle sizes.

gas precursors. The size range of TiO_2 nanoparticles varies from 10 to 35 nm as calculated by the Scherrer formula.

The morphology and structure of these products were investigated by TEM and EDX. Figure 2(*a*) shows that the no. 1 (S1) has good dispersity and uniform sizes of ~10–24 nm. The TEM and inserted EDX images of the random selected particle confirm that there is mainly anatase phase TiO_2 and it also reveals good dispersity. The TEM images of sample 3 (S3) [Figure 2(*c*)] indicate that the S3 possesses good dispersity and relatively uniform sizes ranging from 18 to 40 nm. Figure 2(*c*) exhibits the TEM and EDX images of the randomly selected particles which could be mainly attributed to rutile phase.

Figure 2(*b*) and Table 1 demonstrate that the typical composition of anatase and rutile mixture phase is approximately 50% rutile and 50% anatase (the phase composition ratio of rutile and anatase is adjustable from 99.8% to 99.9%, only partial typical data being shown here). Keeping other experimental conditions fixed, we examined the effect of the gas-phase mixture (the volume ratio of H_2:O_2 and molar ratio of $TiCl_4$:C_2H_6O) precursors. At this lower gas-phase reaction temperature, the rutile phase was not obtained in sample 1. The bar graph based on TEM photos shows that the average size is about 16 (S1), 25 (S2) and 28 nm (S3). With increasing reaction temperature and detonation wave velocity the crystallinity of rutile phase becomes higher, whereas the anatase phase content decreases. In summary, the sphere, polymorphic TiO_2 nanoparticles were formed in the course of the rapid chemical reaction in accordance with the XRD, TEM and EDX results.

Table 1 Synthesis conditions and crystal parameters.[a]

Sample no.	Gas mixture $TiCl_4$:C_2H_6O:H_2:O_2	Component (%)[b]	Grain size[c] (nm)
1	1:0.3–0.6:4:1	A, 99.8; R, 0.20	A, 14.2; R, 30.9
2	1:0.3–0.6:2:1	A, 45.8; R, 54.2	A, 24.2; R, 33.7
3	1:0.3–0.6:2:18	A, 0.10; R, 99.9	A, 19.1; R, 28.4

[a] Initial temperature, 380–420 K. [b] A is anatase, R is rutile. [c] Calculated by the Scherrer formula.

In conclusion, the sphere, high purity and dispersity TiO_2 nanoparticles with a narrow grain size distribution of 10–45 nm have been prepared by a rapid gas-phase reaction. The typical anatase and rutile mixture phase contained approximately 50% rutile and 50% anatase. Under fixed other experimental conditions, the effect of the gas-phase mixture (the volume ratio H_2:O_2 and the molar ratio $TiCl_4$:C_2H_6O) precursors was further regulated and controlled. Increasing reaction temperature and detonation wave velocity affected the proportion between the rutile and anatase phases in the polymorphic TiO_2 powders.

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