Gaseous detonation synthesis and characterization of nano-oxide

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Abstract. Gaseous detonation is a new method of heating the precursor of nanomaterials into gas, and integrating it with combustible gas as mixture to be detonated for the synthesis of nanomaterials. In this paper, the mixed gas of oxygen and hydrogen is used as the source for detonation, to synthesize nano TiO\(_2\), nano SiO\(_2\) and nano SnO\(_2\) through gaseous detonation method, characterization and analysis of the products, it was found that the products from gaseous detonation method were of high purity, good dispersion, smaller particle size and even distribution. It also shows that for the synthesis of nano-oxides, gaseous detonation is universal.

1. Introduction
The concept of nanomaterials was originally proposed by Gleiter of Germany, who had artificially prepared nanocrystals \(^1\) in the 1980s for the first time. When the structure of a material enters the range of nano-scale features, the electronic structure and crystal structure of the crystal surface of the materials have undergone great changes, such as small size effect, surface effect, macroscopic quantum tunneling effect, quantum size effect and dielectric limit domain effects, which shows its broad application prospects in aerospace, chemistry, medicine, biology, electronics and other fields \(^2,3\).

Detonation synthesis is the reaction procedure using the instantaneous high temperature, high pressure and high detonation velocity generated by the detonation, under these extreme conditions, the precursor undergoes pyrolysis, phase transition or chemical reaction with the explosion products. This destroys the structure of the original substance and enables the synthesis of new materials \(^5,6\). Detonation was first used to synthesize nanodiamond \(^7\) and was then extended to synthesize a variety of nanomaterials, including nanoscale TiO\(_2\) and Al\(_2\)O\(_3\) and carbon-encapsulated metal, etc. \(^8,9,10\). Gaseous detonation method directly used gas precursor to turn the precursor into gas, such as using plasma, laser evaporation, electron beam heating, etc, and then detonate the precursor in gas state with the combustible gas, and finally condense and grow into ultra-fine powder during the expansion cooling process of the products; its advantages are that it can reasonably choose the initial condition such as detonation system, regulate the reactive gas species, change the pressure, temperature and density of gas, and choose a strong detonation methods, etc., the nano-powder can be obtained with high purity, good dispersion, even distribution of particle size and small aggregation. In

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In this paper, chlorides were selected as the metal precursor, and H$_2$ and O$_2$ were chosen as the detonation medium to synthesize nano TiO$_2$, nano SiO$_2$ and nano SnO$_2$. The crystalline structure and phase component were obtained on powder X-ray diffraction (XRD) and the evolution of the morphology and particle size of the nano oxide powders was examined by transmission electron microscopy (TEM). As there is no carbon source in gas detonation system, the carbon pollution to nanomaterials which exists in detonation synthesis of conventional explosive was solved.

2. Experimental

2.1. Experimental equipment

Figure 1 is Temperature-control Gaseous Detonation Tube, which is the main experimental equipment for preparing nanoparticles by gaseous detonation method. It is a cylindrical closed container consisting of titanium tube with inner diameter of 100 mm and titanium flange, while being equipped with detonating point, filling port, gas valves and outer loop temperature control system, etc.

![Schematic of detonation tube.](image)

2.2. Experimental procedure

The experimental procedures for the preparation of nano-oxides through gaseous detonation method are basically the same; below is an overview of experimental procedure for preparation of nano TiO$_2$ by gaseous detonation as an example.

Firstly, heat the gaseous detonation tube to 423.15 K to turn the precursor into gas completely by outer loop temperature control system (boiling point of TiCl$_4$ is 409.55 K), vacuumize the tube with a vacuum pump, later inject a certain amount of TiCl$_4$ solution, then observe the pointer changes of the vacuum meter on the detonation tube, and determine the extent for the evaporation of the solution according to variation of the pointer. Subsequently, hydrogen and oxygen are introduced, and their amount can be calculated from the value of the pressure gauge according to Dalton’s Law of partial pressure and the Ideal Gas Law.

Let it stand for 3 to 5 minutes, so that the gas can be completely mixed. Then ignite the mixed gas with detonator and collect the product 15 to 20 minutes later. For the crystal structure of the collected powder particles, XRD-6000 X-ray diffractometer is utilized to carry out polymorph analysis, and the morphology and size of the powder are observed by Tecnai G220 S-Twin TEM.

3. Results and discussion

3.1. Preparation of Nano SiO$_2$

With hydrogen and oxygen as detonation energy, SiCl$_4$ (A Johnson Matthey Company, purity 99%, boiling point: 331.75 K) as precursor, the mixture is heated to 393.15 K and ignited within the detonation tube. Nanoparticles of nano SiO$_2$ are formed with the reaction equation as follows:

$$\text{SiCl}_4(g) + \text{O}_2(g) + 2\text{H}_2(g) \rightarrow \text{SiO}_2(s) + 4\text{HCl}(g) \quad (1)$$
Reactant molar ratio is 1:1:2, and XRD is utilized to carry out analysis for detonation products. The parameters measured are: Cu target (Kα, λ = 0.15406 nm), scanning speed 5°/min, scan range 2θ: 10°-90°.

Figure 2a shows the XRD curve of nano SiO₂ powder, and the product spectrum appears dispersion peak near the diffraction angle of 22°; it is typical amorphous structure, so the product is amorphous particles.

As can be seen from figure 3a, the crystal structure of the product is spherical, mostly in the particle size of 100nm with good dispersibility.

3.2. Preparation of Nano TiO₂
With hydrogen and oxygen as detonation energy, TiCl₄ (sinopharm Chemical Reagent, purity 99%, boiling point: 409.55 K) as precursor, the mixture is heated to 423.15 K and ignited within the detonation tube. Nanoparticles of nano TiO₂ are formed with the reaction equation as follows:

$$\text{TiCl}_4(g) + \text{O}_2(g) + 2\text{H}_2(g) \rightarrow \text{TiO}_2(s) + 4\text{HCl}(g)$$  (2)

Reactant molar ratio is 1:1:2, and XRD is utilized to carry out analysis for detonation products. The parameters measured are: Cu target (Kα, λ = 0.15406 nm), scanning speed 10°/min, scan range 2θ: 10°-80°.

Figure 2b is the XRD curve of nano TiO₂ powder. By comparing with ASTM card, the product prepared is identified as the TiO₂ powder with mixed crystals of anatase phase and rutile phase, where the mass ratio of anatase phase to rutile phase is 45.8:54.2. The particle size is calculated according to Scherrer Equation: $D = \frac{K\lambda}{\beta \cos \theta}$, where $D$ is the crystallite size, $\lambda$ is the wavelength of X-ray radiation (0.154 nm), $\beta$ is the full width at half maximum (FWHM), $\theta$ is the diffraction angle, and K is usually taken as 0.89. The calculated result is anatase phase being 26.24 nm and rutile phase being 36.77 nm.

As can be seen from figure 3b, the product crystal is spherical with particle size mostly of 80-100 nm, and there are also particles with diameter of 150 nm, but the products are of good dispersibility.

3.3. Preparation of Nano SnO₂
With hydrogen and oxygen as detonation energy, SnCl₄ (Sinopharm Chemical Reagent, purity: 99%, boiling point: 387.25 K) as precursor, the mixture is heated to 393.15 K and ignited within the detonation tube. Nanoparticles of nano SnO₂ are formed with the reaction equation as follows:

$$\text{SnCl}_4(g) + \text{O}_2(g) + 2\text{H}_2(g) \rightarrow \text{SnO}_2(s) + 4\text{HCl}(g)$$  (3)

![Figure 2. XRD diagrams (a) SiO₂; (b) TiO₂; (c) SnO₂.](image-url)
Reactant mole ratio is 1:1:2, and XRD is utilized to carry out analysis for detonation products. The parameters measured are: Cu target (Ka, $\lambda = 0.15406$ nm), scanning speed 5°/min, scan range 2θ: 10°-70°.

Figure 2c is the XRD diagram of the collected product, where the main component is found to be SnO$_2$. All the peaks of SnO$_2$ can be observed in figure 2c, and the small peaks of Cl is also found, which may be due to the incompletely reacted liquefied SnCl$_4$. According to Scherrer Equation, the average particle size of detonation products is calculated to be 8.2 nm.

![Figure 3: TEM images of the three samples (a) SiO$_2$; (b) TiO$_2$; (c) SnO$_2$.](image)

Figure 3c is the topography observed from TEM. It can be seen that the product particles are spherical, of even size ranging between 1-10 nm, which is in line with the XRD analysis. The lattices crystal grains are clearly visible, without obvious aggregation, and the product particles are of good dispersibility.

4. Conclusion
This paper has prepared nano SiO$_2$, nano TiO$_2$ and nano SnO$_2$ by gaseous detonation method, the products’ particles are spherical; the size is even and they show good dispersibility. It is concluded that
using gaseous detonation method to synthesize nano-oxides is feasible and universal.

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