

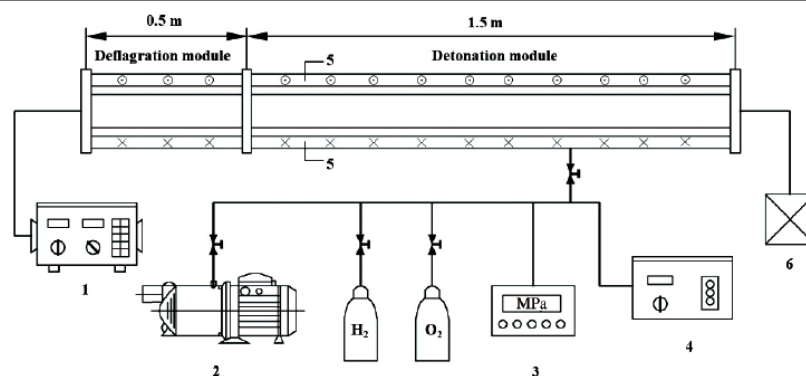
Gaseous-Liquid Detonation Controllable Synthesis of Polycrystalline Nanostructure TiO₂ and TiO₂@Carbon Composites

Ning Luo, Yinmei Cao
China University of Mining and Technology
Xuzhou City, Jiangsu Province, China

1 Author instructions for 29th ICDERS Extended Abstracts

Here we demonstrate a simple, rapid for the controlled synthesis of polycrystalline nano-TiO₂ and core-shell structural carbon coated TiO₂ nanoparticle by the gaseous-liquid detonation (GLD) method using CH₄, O₂, C₆H₆, H₂ and TiCl₄ as the mixture precursors in milliseconds. The nanocrystal structures, components, particle size, and morphology were characterized by the Various techniques, including XPS, TEM, XRD and Raman. The results demonstrate that the nano-TiO₂ consists of pure anatase-TiO₂, pure rutile-TiO₂, and the mixtures of spherical or quasi-spherical morphologies with particle size of 20~150 nm. Furthermore, the formation mechanism of nano-TiO₂ by GLD method was analyzed. The relevant GLD parameters were calculated based on the C-J theory and the related chemical reaction data, which effectively verifies the influence of different molar ratios of precursors and initial pressures on the controllable synthesis of polycrystalline nano-TiO₂. On the other hand it is also found that the sphere, good disperse mixed crystal TiO₂ nanoparticles with crystal size of 10-30 nm were coated with thick graphite layers. Based on Zeldovich Neuman-Doring (ZND) model, the detonation synthesis mechanism of core-shell structure TiO₂@C is discussed. This rapid synthesis method can be extended to the preparation of other core-shell materials.

2 Experimental



1-high energy igniter; 2-vacuum pump; 3-barometer; 4-liquid atomizing system; 5-temperature control system; 6-exhaust gas treatment equipment

Fig.1 Schematic diagram of GLD system

In a typical preparation procedure, the GLD tube was heated to 380~550 K after vacuuming barometer reading-0.09 MPa). A certain amount of TiCl_4 solution was injected by the atomizer into the tube. Then the mixed gas with a certain proportion of H_2 and O_2 was pumped into the GLD synthesis system until reaching the atmosphere pressure. The gaseousliquid mixtures were placed statically for 5~10 min and then ignited using the electric igniter of 20~40 J. Finally, after the tube was cooled down to room temperature, the white products were collected from the inner wall of GLD tube and washed with absolute ethanol.

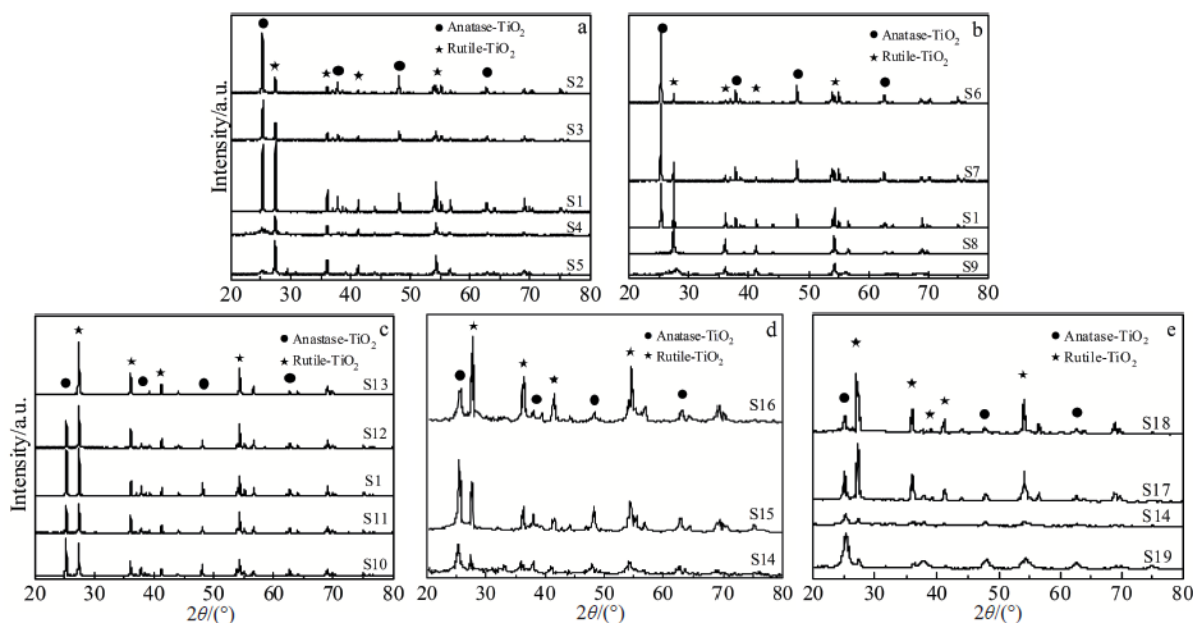


Fig.2 XRD patterns of S1~S5 (a), S6~S9 (b), S10~S13 (c), S14~S16 (d), and S17~S19 (e) specimens

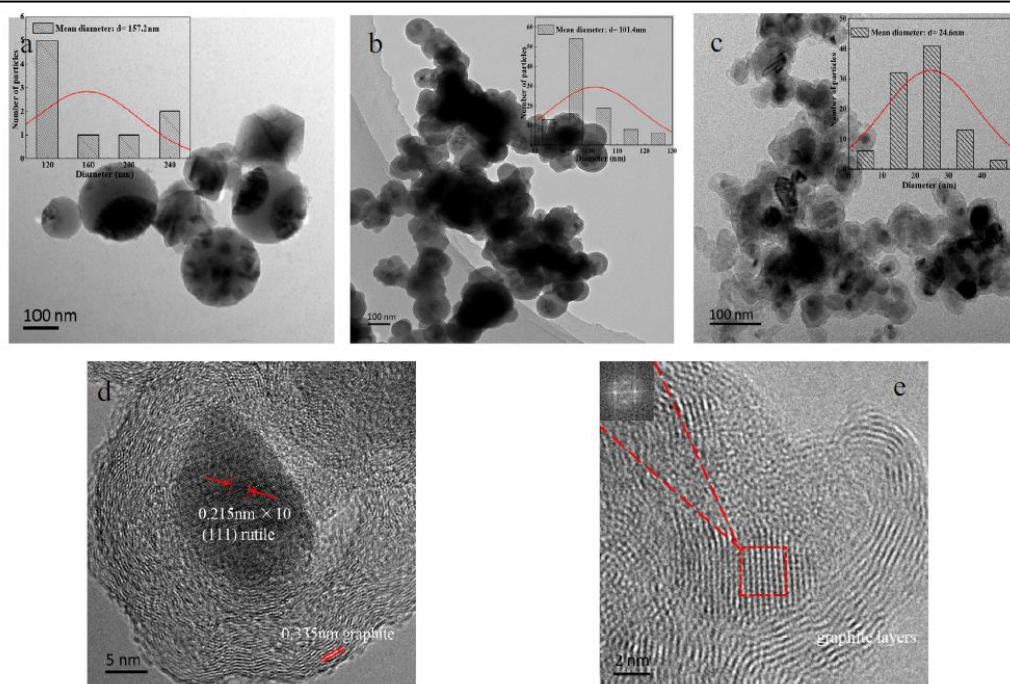


Fig.3 TEM image of (a) 1# carbon-free, (b) 2# carbon-low and bar chart of diameters, (c) 3# carbon-rich and bar chart of diameters (d) 3# HRTEM image of coreshell structure, (e) 3# HRTEM image and the FFT pattern

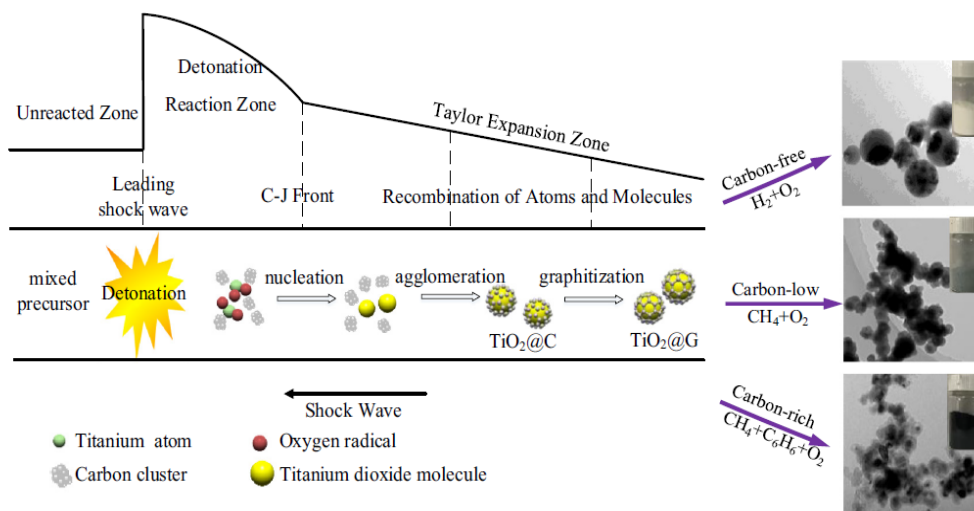


Figure 4 Scheme illustration of the formation process of $\text{TiO}_2@\text{G}$

After the detonation wave is swept, the mixed precursor become detonation product under high temperature and high pressure. In this special environment, the molecules and atoms recombine to form new materials. The intermediate compounds of detonation are extremely plentiful in the C-J plane and inter-collision between free atoms facilitates the nucleation of nanoparticles at high temperature and pressure. Ti and O atoms were firstly interconnected to nucleation and carbon atoms are dissolved and diffused into the exterior of crystalline TiO_2 . In Taylor expansion zone, the excess free carbons enter

the graphite phase under the effect of wasted heat. The highly energetic substances with fast reaction rates and chemical reactions can be in gaseous or liquid form. During the whole gas-liquid detonation reaction, the content of carbon is critical to the formation of the core-shell structure. It is necessary to construct a carbon-rich environment to synthesize a graphite-coated structure. When we used CH₄, O₂, and TiCl₄ as precursors, most of the TiO₂ was not coated. Therefore, we increase the carbon content of the precursor by adding C₆H₆. Meanwhile, the combustion of C₆H₆ emit a large amount of heat, which promotes the formation of graphite structure.

References

- [1]Luo N, Li X, Wang X, Yan H, Zhang C, Wang H. (2010). Synthesis and characterization of carbon-encapsulated iron/iron carbide nanoparticles by a detonation method, Carbon 48(13): 3858–3863.
- [2]Luo N, Liu KX, Li X, Shen H, Wu S, Fu Z, (2012). Systematic study of detonation synthesis of Ni-based nanoparticles, Chem. Eng. J. 210: 114–119.
- [3]Luo N, Xiang JX, Liang HL, Sun X, Ma ZG, Yang WH, Jing HW. (2019).Rapid gas-liquid detonation synthesis of core-shell structural graphite coated TiO₂ nanoparticles, Diam. Relat. Mater., 92:61-64.
- [4]Luo N, Sun X, Fan XR.(2022).Controllable Synthesis of Polycrystalline Nanostructure TiO₂ by Gaseous-Liquid Detonation Method. Rare Metal Mat. Eng., 51(01): 119-126.