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ARTICLE

Preparation of Nano-ZrO_2 Powder and Properties of Its Aqueous Suspension

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Abstract: Nanometer-sized zirconia (ZrO_2) powder was synthesized from $ZrOCl_2 \cdot 8H_2O$ through a hydrothermal method. The aqueous suspension stability of ZrO_2 powder was studied by zeta potential measurement and particle size analysis. Results show that ZrO_2 nanoparticles are ellipsoidal with uniform particle size, and the particle size is mainly in the range of 40–100 nm. The isoelectric point (IEP) occurs at pH=9.0. ZrO_2 particles are well dispersed far from IEP and severely agglomerated near IEP.

Key words: ZrO_2 powder; zeta potential; aqueous suspension; hydrothermal method

ZrO_2-based materials have unique physical and chemical properties. They have been widely used in solid oxide fuel cells, thermal barrier coatings, oxygen sensors, adsorbents and other fields. In contrast, nanocrystalline ZrO_2-based materials have enhanced mechanical, thermal, electrical and optical properties[1–7]. These materials are generally prepared from nanopowder, so it is vital to synthesize nanometer-sized powder with uniform particle size and high purity, which should be superfine and non-agglomerated[8].

Nanocrystalline coatings are usually prepared by a suspension of nanopowder. For example, the suspension plasma spraying (SPS) first uses nanopowder as starting material to prepare suspension and then this suspension was fed into the plasma torch. ZrO_2-based coatings prepared by SPS have nanometer-sized grains and high bonding strength with the substrate, which can effectively improve the coating properties[6, 9–11]. However, coatings' properties depend to a large extent on the suspension feedstocks' properties, especially the dispersion of powder in the liquid carrier[8]. Similarly, the electrophoretic deposition (EPD) process also uses suspension to prepare coatings. The charged particles suspended in the liquid medium are attracted by the external electric field and deposited on the conductive substrate. Nanocrystalline ZrO_2-based coatings prepared by EPD have been applied in many areas, and the properties of the suspension are also crucial to control the electrophoretic processes[12–16]. Therefore, measuring suspension properties is a prerequisite to realize these preparation techniques. The suspension stability of nanopowder can be assessed by zeta potential measurement. The higher the zeta potential of particles in the suspension, the more stable the suspension[9,14–17]. Analysis on the relationship between powder's zeta potential and particle size plays an auxiliary role in characterizing the suspension properties.

In this study, nanometer-sized ZrO_2 powder was synthesized by a one-step hydrothermal method using zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) as the starting material. The phase analysis and morphology characterization of the prepared powder were performed by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). By dispersing the nanometer-sized ZrO_2 powder in aqueous solutions, the powder's zeta potential and particle size were measured as a function of the pH to study the stability of the suspensions, which was expected to investigate and to optimize the properties of ceramic suspensions.

1 Experiment

1.1 Preparation of ZrO_2 powder

The starting material was $ZrOCl_2 \cdot 8H_2O$ (>99%, Shanghai Macklin Biochemical Co., Ltd). First, 2.4169 g $ZrOCl_2 \cdot 8H_2O$ was dissolved into 50 mL deionized water. After stirring

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vigorously for about 1 h, the solution was transferred to a hydrothermal autoclave and reacted at 413 K for 4 h. The precipitates were collected and washed 4 times with deionized water until all the unreacted $ZrOCl_2·8H_2O$ was removed. The obtained precipitates were dried at 353 K for 12 h, and the ZrO_2 powder was created.

1.2 Characterization

The phase structure of the powder was determined by XRD with Cu Kα radiation (D/max 2500/PC; Rigaku, Japan). FESEM (SU8220; Hitachi, Japan) was used to identify the morphology of the powder. Before imaging, the sample was sputtered with gold under vacuum for 200 s (JEC-1600 auto fine coater; JEOL, Japan). The microstructure of the powder was observed by TEM (Talos F200X; FEI, USA). The nanoparticle size analyzer (90Plus Zeta; Brookhaven, USA) was used to measure the powder's particle size distribution based on the principle of dynamic light scattering (DLS).

1.3 Zeta potential measurements

An aqueous suspension of 0.2 mg/mL ZrO_2 powder was used to measure the zeta potential. And the suspension pH was adjusted by adding dilute solutions of NaOH and HCl. After ultrasonic treatment for the suspension for 10 min, a zeta potential analyzer (90Plus Zeta; Brookhaven, USA) was used to measure the zeta potential of the powder by the electrophoresis light scattering (ELS) method.

2 Results and Discussion

2.1 ZrO_2 powder characterization

Fig. 1 shows the XRD pattern of ZrO_2 powder synthesized by hydrothermal process. The XRD peaks reveal that ZrO_2 is the monoclinic phase, which can be indexed according to PDF #86-1451, indicating that the hydrothermal method can directly get crystalline oxides from an aqueous solution.

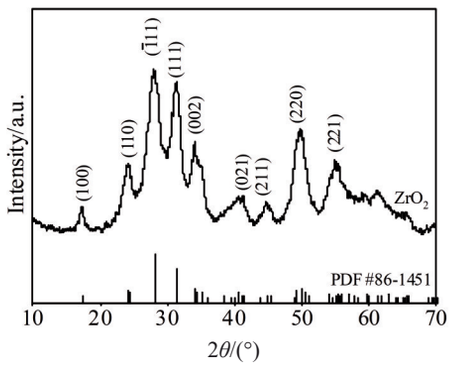

Fig.1 XRD pattern of ZrO_2 powder

During the hydrothermal reaction, $ZrOCl_2·8H_2O$ first hydrolyzes to form $Zr(OH)_4$ and HCl, and finally $Zr(OH)_4$ transforms into ZrO_2 and H_2O. The formation mechanism is as follows[18]:

$$ZrOCl_2·8H_2O + 3H_2O \rightarrow Zr(OH)_4 + 2HCl \quad (1)$$

$$Zr(OH)_4 \rightarrow ZrO_2 + 2H_2O \quad (2)$$

Fig. 2a shows the FESEM morphology of ZrO_2 powder. Fig.2b and 2c show the TEM images of ZrO_2 powder in lower and higher magnifications, respectively. It is observed that ZrO_2 particles have an ellipsoidal morphology. The powder is in nanometer size with uniform particle size and good dispersion. The high-resolution TEM (HRTEM) image of ZrO_2 powder in Fig. 2d shows well-resolved lattice fringes. The lattice fringe spacing is 0.28 nm, equal to the spacing of (111) planes in monoclinic ZrO_2. The analysis of selected area electron diffraction (SAED) pattern (Fig. 2e) further proves that the ZrO_2 powder is a monoclinic structure, and the polycrystalline diffraction rings correspond to the (111), (002) and (211) planes of monoclinic ZrO_2. It is observed from the

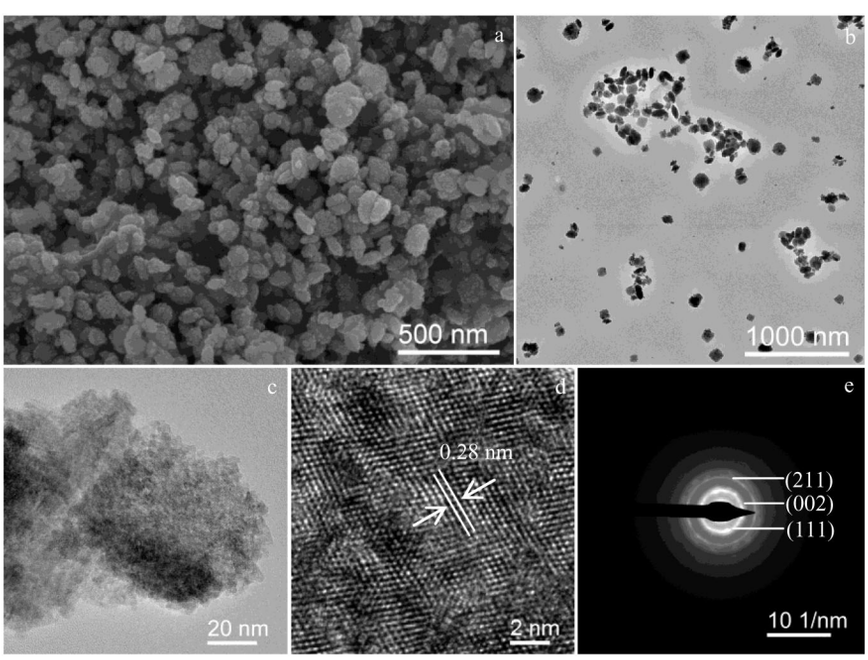

Fig.2 FESEM morphology (a), TEM images (b, c), HRTEM image (d), and SAED pattern (e) of ZrO_2 powder

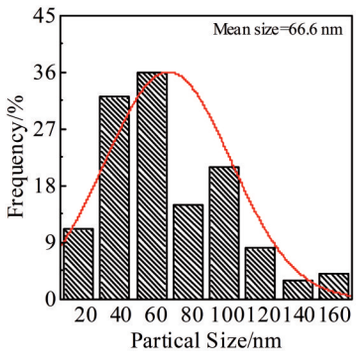

Fig.3 ZrO_2 particle size distribution measured from the TEM image

histogram (Fig. 3) that the size of ZrO_2 particles is mainly in the range of 40–100 nm, with a mean value of 66.6 nm. For coating preparation with suspensions, such as SPS and EPD, it is beneficial to use small and uniform powder, because powder with small particle sizes will carry out Brownian motion and can suspend for a long time in a liquid medium to form a stable suspension[16].

2.2 Properties of ZrO_2 suspension

The zeta potential of ZrO_2 in aqueous solutions at different pH values is shown in Fig.4. It can be seen that when pH<9.0, the zeta potential is positive. The zeta potential value gradually increases when the pH value drops from 9.0 to 3.0. At pH=3.0, the zeta potential value reaches the maximum of 33.29 mV. This is because, for metal oxides powder dispersed in water, the hydration layer on the surface is composed of a large number of amphoteric hydroxyl groups, which can readily adsorb H^+ or OH^- ions on its surface[19]:

$$(M-OH)_{(Surface)} + H^+ = (M-OH_2)^+_{(Surface)} \quad (3)$$

$$(M-OH)_{(Surface)} + OH^- = (M-O)^-_{(Surface)} + H_2O \quad (4)$$

With the addition of HCl, the pH value of the suspension decreases, and more H^+ is adsorbed on the surface of ZrO_2, which makes the particle surface positively charged and increases the zeta potential of ZrO_2. However, the zeta potential value decreases when the pH drops from 3.0 to 2.6. This is because more HCl is needed to adjust the pH value for strongly acidic conditions. The introduction of a large number of ions compresses the thickness of the double electric layer, thus reducing the zeta potential of the powder. A similar phenomenon is observed at pH>9.0, except that ZrO_2 particles adsorb OH^- in the suspension and are negatively charged. At pH=11.6, the zeta potential value is –33.03 mV. The point where the zeta potential value is 0 is the isoelectric point (IEP), and the IEP occurs at pH value of ~9.0.

The size distribution for ZrO_2 powder in the aqueous suspension is measured as a function of pH by the dynamic light scattering method. As shown in Fig. 5, the average particle size of ZrO_2 powder is in the range of 175–214 nm under the conditions of pH<8.0 and pH>10.0. Compared with the previous FESEM and TEM results, it can be concluded that the agglomeration between particles is not apparent. The average particle size of ZrO_2 power changes with the change of solution pH, which agrees with the zeta potential results. According to DLVO theory, there are two force interactions between single suspended particles: electrostatic force and van der Waals force. The higher the zeta potential, the greater the electrostatic repulsion force between particles, so the particles are unlikely to agglomerate[16]. Therefore, the average particle size decreases as the pH value drops from 8.0 to 3.0. At high (>11.6) and low (<3) pH levels, a moderate increase in average particle size occurs. This is an anticipated consequence of the decrease in zeta potential of the powder. Similar results have also been reported by other researchers[14]. When the pH value reaches 9.0 (IEP), the average particle size reaches 3281.5 nm, indicating that the particles are severely agglomerated.

Fig.6 shows that ZrO_2 powder in the suspension with a pH value of 9.0 settles rapidly, forming many low-density and weakly adherent deposits at the bottom of the container. However, under other pH conditions, ZrO_2 powder in the suspension flocculates less and settles slowly. After 12 h or even longer, only a small amount of dense and robust adherent

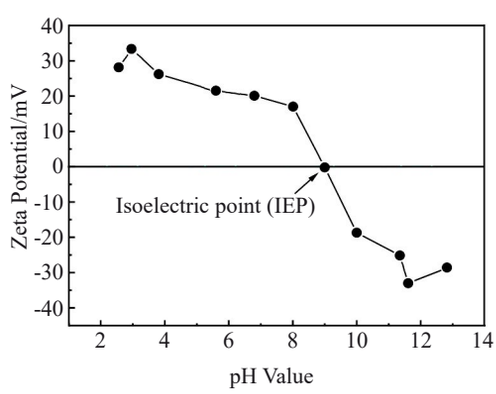

Fig.4 Zeta potential of ZrO_2 under different pH conditions

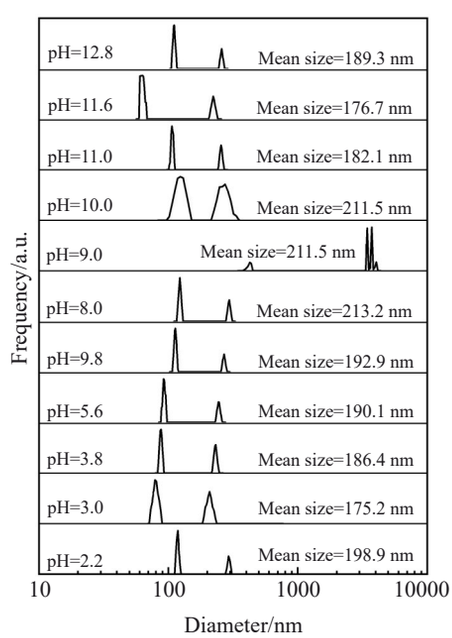

Fig.5 Size distribution of ZrO_2 powder as a function of pH

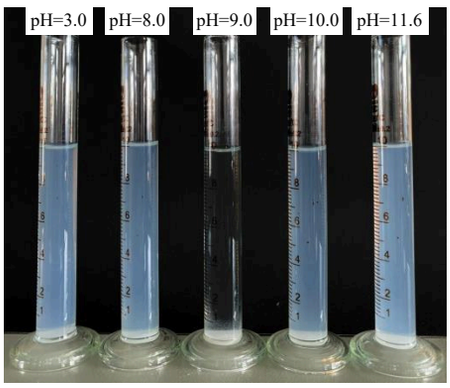

Fig.6 ZrO_2 suspensions left for 12 h in different pH conditions

deposits are formed at the bottom of the container. These results correspond to the zeta potential analysis. Under different pH conditions, the aggregate sizes are different due to different zeta potentials of particles. The aggregates with small sizes suspend for a long time due to Brownian motion, while large aggregates settle due to gravity, causing instability of the suspension. For the ZrO_2 powder prepared in this work, the zeta potential value of ~17 mV is sufficient to stabilize the suspension.

3 Conclusions

1) The monoclinic nano-ZrO_2 powder can be prepared by hydrothermal method using $ZrOCl_2·8H_2O$ as raw material. The ZrO_2 nanoparticles are ellipsoidal with uniform size, which is mainly distributed at 40–100 nm.

2) The isoelectric point occurs at pH value of ~9.0. At this pH, the ZrO_2 particles agglomerate seriously, and the aggregate size reaches 3281.5 nm.

3) The stability of the suspension is related to the solution pH. The suspension at pH=9.0 has poor stability. While under other pH conditions, the suspensions have good dispersion of the ZrO_2 nanoparticles, and nanoparticles in these suspensions flocculate less and settle slowly. For the ZrO_2 powder prepared in this work, the zeta potential value of ~17 mV is sufficient to stabilize the suspension.

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纳米ZrO_2粉体的制备及其水悬浮液性能

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摘 要：以$ZrOCl_2·8H_2O$为锆源，通过水热法合成了纳米二氧化锆（ZrO_2）粉体。结果表明，ZrO_2颗粒为椭球形，粒径主要在40~100 nm范围内，粒径分布窄。通过测量ZrO_2的Zeta电位和粒径，研究了不同pH条件下水悬浮液中此ZrO_2粉体的表面电荷和分散性能。发现ZrO_2粉体的等电点（IEP）为pH=9.0，在远离IEP处ZrO_2颗粒分散性好，而在IEP处则团聚严重。

关键词：ZrO_2粉体；Zeta电位；水悬浮液；水热法

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