ABSTRACT
Monodisperse and pure phase zirconia (tetragonal: T-ZrO$_2$; monoclinic: M-ZrO$_2$) nanocrystals with finely tuned sizes as well as ultrathin T-ZrO$_2$ nanowires have been selectively synthesized by a facile solvothermal method. For the first time, a diagram of the size to effective strain was mapped for both T-ZrO$_2$ and M-ZrO$_2$, which gives a good explanation for the size- and cation doping-dependent stability of the two phases on the sub-10 nm scale. This work may expand our understanding of the phase properties of not only zirconia, but also various other polymorphic nanocrystals.

KEYWORDS
Nanocrystals, polymorphism, phase stability
size, and morphology are required. Hyeon et al. reported a nonhydrolytic sol–gel reaction between zirconium(IV) n-propoxide and zirconium(IV) chloride at 340 °C to synthesize monodispersed tetragonal (T-ZrO₂) nanocrystals [30]. Zhao et al. developed a two-phase approach for the synthesis of shape-controlled zirconia nanocrystals from zirconium(IV) n-propoxide, but the product suffered from the presence of polymorphs: both monoclinic and tetragonal phases co-existed [31]. Therefore, the synthesis of monodisperse pure-phase T-ZrO₂ and monoclinic (M-ZrO₂) nanocrystals with good size controllability is urgently required. In this paper, we report a new single-phase solution method to synthesize monodisperse pure T-ZrO₂ and monoclinic (M-ZrO₂) nanocrystals with finely tuned sizes, as well as T-ZrO₂ ultrathin nanowires. The stabilization of T-ZrO₂ with yttrium(III) doping was also investigated. The resulting materials show unique phase related size–strain features.

1. Experimental

1.1 Preparation of zirconyl oleate

1.6 g of ZrOCl₂·8H₂O (AR, Sinopharm Chemical Reagent Co.) was dissolved in 10 mL of deionized H₂O to form solution A; 3.1 g of sodium oleate (> 98%, Beijing Chemical Reagent Co.) was ultrasonically dissolved in 20 mL of deionized H₂O and 25 mL of ethanol (AR) to form solution B. Then solutions A and B were mixed. Excess cyclohexane (40 mL) was added in order to extract zirconyl oleate, with stirring for 20 min. The upper organic layer was separated, the cyclohexane was distilled off, and the residue washed with water and dried to give zirconyl oleate. Yttrium oleate was prepared in a similar way by using Y(NO₃)₃·6H₂O.

1.2 A typical synthesis of M-ZrO₂ nanocrystals

0.5 g of zirconyl oleate was dissolved in a mixture of 0.4 mL of oleic acid, 1 mL of oleylamine, and 10 mL of n-octane (AR). The mixture was allowed to react at 200 °C for 2 days. The sizes of the M-ZrO₂ nanocrystals can be tuned from 3.0 nm to 0.8 nm by shortening the reaction time from 2 days to 4 h. When n-butanol was used in place of ethanol, flower- or string-like M-ZrO₂ nanocrystals structures were obtained. The influence of the chain length of the alcohol on the phase of ZrO₂ obtained is discussed below.

1.3 Synthesis of T-ZrO₂ nanocrystals

0.5 g of zirconyl oleate was dissolved in a mixture of 8 mL of oleic acid, 1 mL of oleylamine, and 10 mL of n-octane (AR). The mixture was allowed to react at 200 °C for 2 days. The sizes of the T-ZrO₂ nanocrystals can be tuned from 3.0 nm to 0.8 nm by shortening the reaction time from 2 days to 4 h. Using n-hexanol in place of ethanol also yielded T-ZrO₂ nanocrystals.

1.4 Synthesis of T-ZrO₂ ultrathin nanowires

0.5 g of zirconyl oleate was dissolved in a mixture of 1 mL of oleylamine and 10 mL of cyclohexane. The mixture was reacted at 200 °C for 3 days. The white gel-like product was ultrasonically washed with cyclohexane.

1.5 Synthesis of yttrium doped T-ZrO₂ nanocrystals

An appropriate amount of yttrium oleate was added to the system used to synthesize M-ZrO₂ nanocrystals.

1.6 Characterization

The phase purity of the products was verified by powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å). The sizes and morphologies of the nanocrystals were measured using a JEOL JEM-1200EX transmission electron microscope (TEM) at 120 kV, and a Tecnai G2 F20 S-Twin high-resolution transmission electron microscope (HRTEM) at 200 kV. UV-vis absorption spectra were measured on a Hitachi U-3010 spectrophotometer. Photoluminescence (PL) spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer. FT-
IR spectroscopy was performed using a Nicolet 560 spectrometer.

2. Results and discussion

2.1 Phase and structure characterization

TEM and HRTEM images of the M-ZrO$_2$ nanocrystals, T-ZrO$_2$ nanocrystals, and T-ZrO$_2$ ultrathin nanowires are shown in Fig. 1. The XRD patterns indicate that both the M-ZrO$_2$ and T-ZrO$_2$ nanocrystals/nanowires are phase pure, agreeing well with JCPDS # 88-2390 and JCPDS # 80-0965, respectively. The T-ZrO$_2$ ultrathin nanowires are curved and branched in morphology and have broadened XRD peaks, indicating an ultra-small diameter. Measured from the HRTEM images (see Figs. 1(g) and 1(h)), the average diameter of the T-ZrO$_2$ nanowires is ~1.2 nm, consistent with the XRD result. The M-ZrO$_2$ nanocrystals are irregular in shape, while the T-ZrO$_2$ nanocrystals have a relatively spherical shape. The sizes of the M-ZrO$_2$ and T-ZrO$_2$ nanocrystals can be tuned from 8.0 nm to 2.8 nm, and 3.0 nm to 0.8 nm, respectively, by shortening the reaction time from 2 days to 4 h. Based on the formalism of Filipovich and Kalinina [32], Garvie, Mitsuhashi, Bailey, et al. predicted that T-ZrO$_2$ (as spherical crystals) should be the stable phase (not metastable) below a critical size of about 10 nm at 298 K [33-38]. However, our results show that, both pure T-ZrO$_2$ and M-ZrO$_2$...
nanocrystals within this size limit can be stabilized at ambient temperature, indicating that special stabilizing mechanisms are in operation. The fine controllability of the nanocrystal sizes of pure phase T-ZrO$_2$ and M-ZrO$_2$ in the range < 10 nm gives an ideal opportunity to probe deeper into the physics of the nano size-related phase transformation/stability.

2.2 Control of morphology: Effect of acid and amine

In the synthesis of ultrathin T-ZrO$_2$ nanowires, only oleylamine (without oleic acid) was utilized as the capping agent. By controlling the reaction time, it was found that the formation of the nanowires followed a typical oriented attachment growth mechanism. In the primary stage, T-ZrO$_2$ nanocrystal seeds were incubated. Then the seeds aggregated and attached. Finally, the ripened nanowires came into being. When a smaller amount of oleic acid (0.1 mL) was used in place of that (0.4 mL) required to synthesize T-ZrO$_2$ nanocrystals in n-octane with the same amount of oleylamine (1 mL), a pearl-string like structured T-ZrO$_2$ appeared (Figs. 2(d) and 2(e)), which we believe is an intermediate stage in the synthesis of the ripened nanowires. It probably arises because the oleylamine was selectively anchored to some specific T-ZrO$_2$ surfaces (or capping less tightly to some faces), facilitating the oriented attachment along the less capped crystal planes; the oleic acid was less sensitive to different nanocrystal planes and capped all the surfaces indiscriminately (or capping more tightly), therefore, prohibiting the attachment of other seeds and resulting in the formation of dispersed nanocrystals instead of the ultrathin nanowires. This is consistent with the Derjaguin–Landau–Verwey–Overbeek (DLVO) model, which states that higher surface covering ratios of ligands lead to larger steric repulsion between nanocrystals, and therefore the oriented attachment is weakened [39-43]. The increase in size (compare Figs. 1(g), 1(h) and Figs. 2(d), 2(e)) confirms this hypothesis: under conditions of less capping, the nucleation is boosted; in contrast, under conditions of strong capping and/or longer chain solvents, the nucleation is retarded and growth dominates. The schematic mechanism is shown in Fig. 2(f). The selective capping property of oleylamine has also been suggested as a reason for the formation of other ultrathin nanowires, e.g., SnO$_2$, InOOH, and Au [44-46]. The FT-IR measurements also provide supporting evidence (Figs. 2(g) and 2(h)). The C=O stretching vibration mode at 1738 cm$^{-1}$ was clearly observed in the FT-IR spectrum of T-ZrO$_2$ nanocrystals, which were synthesized in the oleic acid-containing system. The peak shifts from that of free oleic acid at 1708 cm$^{-1}$, indicating the coordination interaction with the nanocrystals. The bands in the range 2800-3000 cm$^{-1}$ are the CH$_3$ symmetric and asymmetric stretching vibrations. The broad peak at ~3400 cm$^{-1}$ is assigned to absorbed H$_2$O or O–H groups. The multiple peaks in the range 1000-1700 cm$^{-1}$ can be assigned to the N–H, C–H, COO$^-$, and H$_2$O modes or their mixtures. The strong peaks in the range 400-700 cm$^{-1}$ are Zr–O vibration modes.

2.3 Phase control: Effect of alcohols with different chain length

By introducing ethanol into the system, we found that pure monoclinic phase zirconia nanocrystals were obtained. Zhao and co-workers have previously reported that, when increasing the hydrocarbon chain length of the capping agents (carboxylic acids), the fraction of monoclinic zirconia decreased [31]. In our synthesis system, a similar effect was found in that, when substituting ethanol with a longer chain alcohol (n-hexanol), pure tetragonal phased zirconia nanocrystals were obtained. This suggests that the formation of either a tetragonal or a monoclinic phase was determined by different reaction kinetic process. The pyrolysis of zirconyl oleate yields T-ZrO$_2$, while the alcohol-induced esterification and hydrolysis reactions prevail [44, 47], M-ZrO$_2$ is obtained. When shortening the reaction time, only an amorphous precursor (neither T-ZrO$_2$ nor M-ZrO$_2$) could be separated before M-ZrO$_2$ nucleation. The results differ from the size-related T-ZrO$_2$–M-ZrO$_2$ martensitic transformation that was indicated in the two-phase synthesis system, in which the M-ZrO$_2$ volume fraction increased with increasing size during the reaction stages [31]. This suggests an alternative mechanism in which the reaction-growth type (pyrolysis vs. esterification/hydrolysis) could be responsible for the T-ZrO$_2$ or M-ZrO$_2$ nucleation;
this is further supported by the size–strain analysis discussed below. Otherwise, the T-ZrO₂ nucleation and martensitic transformation will be triggered instantaneously and essentially simultaneously such that they can hardly be separated. When n-butanol, an alcohol with medium chain length, was used, the as synthesized M-ZrO₂ nanocrystals tended to attach to form flower- or string-like structures, as shown in Figs. 2(a)–2(c). This can be understood in terms of the effective dielectric constant tuned attachment mechanism [44].
2.4 Doping-induced phase stabilization

It has long been recognized that the polymorphism of zirconia can be tuned by cation doping (Y³⁺, Yb³⁺, Ca²⁺, Mg²⁺, Ce⁴⁺, etc.) [48, 49]. Of these, yttrium(III) is widely used as a stabilizer of the tetragonal phase. When yttrium oleate was introduced into the typical M-ZrO₂ synthesis system, yttrium-stabilized T-ZrO₂ nanocrystals were obtained. The TEM image is shown in Fig. 3(a) and the X-ray energy dispersive spectra (EDS) in Fig. 3(b) confirm that the yttrium content increases with the doping level. A similar stabilization was achieved when using lanthanide ions (e.g., Eu³⁺, Yb³⁺). The XRD peaks undergo a gradual broadening and a shift to the small angle direction when the Y³⁺ doping level increases from 2% to 30% (cation ratio, ±1.2% from the EDS quantitative analysis), indicating a decrease of crystallite size and increase of lattice constant, respectively (Figs. 3(c)–3(e)). This is consistent with the fact that the radius of Y³⁺ (0.102 nm) is larger than that of Zr⁴⁺ (0.084 nm). The monoclinic phase was retained when yttrium oleate is added in the ripening stage of M-ZrO₂. Therefore, the ion doping must occur during the ZrO₂ nucleation and growth stages.

2.5 Dissolution–recrystallization phase transformation

The T-ZrO₂ to M-ZrO₂ transformation was also revealed by hydrothermally treating T-ZrO₂ nanocrystals at 200 °C under basic conditions (NaOH: 1–5 mol/L). The as formed M-ZrO₂ nanocrystals have a size of 20–100 nm. The dissolution–recrystallization mechanism is believed to be responsible for the phase transformation.

2.6 Strain in zirconia nanocrystals

The existence of different nanocrystal phases at room temperature depends on two aspects. One is the historical kinetic factor in the nucleation-

![Figure 3](image-url)

**Figure 3** (a) TEM image of the yttrium doped T-ZrO₂ nanocrystals. (b) EDS spectrum showing a 30% Y-doping, with the insert showing Y-doping of 2%, 10%, and 30%. (c)–(e) XRD patterns showing the shift of diffraction peaks to small angle with the increasing doping fraction of yttrium.
growth stages; the other is the thermodynamic principle. The former is often associated with non-equilibrium growth processes, while the later is mainly governed by the total energies of the surface and bulk, and the strain. Holmes et al. measured the heat of immersion of T-ZrO$_2$ and M-ZrO$_2$ prepared by calcining zirconium hydroxide in the range 600–1000 °C. They concluded that M-ZrO$_2$ has a higher surface energy [34]. The heat of the T-ZrO$_2$–M-ZrO$_2$ transformation/unit volume and transformation temperature is also known. Garvie et al. indicated that T-ZrO$_2$ should be a more stable phase than M-ZrO$_2$ below a critical particle size of 10 nm at temperatures much lower than the bulk transformation temperature [37]. However, our results showed that not only pure T-ZrO$_2$, but also pure M-ZrO$_2$ nanocrystals, can be synthesized within this size limit and stabilized at room temperature. Therefore, the third factor—the intrinsic strain—should be taken into account.

The Williamson–Hall equation was applied to deduce the effective strain from the XRD data [50–52]:

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{\delta} + \frac{2\eta \sin \theta}{\lambda}$$

(1)

where $\theta$ is the Bragg angle of the peak, $\lambda$ is the X-ray wavelength, $\delta$ is the effective particle size, $\eta$ is the effective strain, and $\beta$ is the full width at half maximum (FWHM, in radians) estimated by the following equation:

$$\beta = \frac{\beta_{1/2} - \beta_p}{0.89}$$

(2)

where $\beta_{1/2}$ and $\beta_p$ are the FWHMs obtained for nanocrystals and micron-sized powders, respectively. Here $\beta_p = 0.25^\circ$ is taken as a constant. $\beta_{1/2}$ is extracted from the XRD patterns by Lorentzian multi-peak fitting. To extract the effective strain ($\eta$) from the XRD patterns, (101), (112), and (211) peaks were selected for T-ZrO$_2$, and (-111), (111), and (220) were selected for M-ZrO$_2$. An approximation was made that very adjacent XRD peaks have the same FWHM value. For T-ZrO$_2$, we assumed FWHM$_{(112)} = $FWHM$_{(200)}$, FWHM$_{(211)} = $FWHM$_{(400)}$, and for M-ZrO$_2$, we assumed FWHM$_{(212)} = $FWHM$_{(022)} = $FWHM$_{(202)} = $FWHM$_{(122)} = $FWHM$_{(-221)}$. No shape factor of the nanocrystals was included. The Scherrer equation was applied to calculate the nanocrystal size, using the Lorentzian multi-peak fitting data $\beta_{1/2}$ and $\theta$. For T-ZrO$_2$, the size is the average value of (101), (112), and (211); for M-ZrO$_2$, the size is the average value of (111) and (-111).

A negative slope ($\eta$) of the linear fit of $\beta \cos \theta$ to $2 \sin \theta$ is indicative of compressive strain. The calculated nanocrystal size and the effective strain ($\eta$) are mapped in Fig. 4(c) (The calculation data can be found in Table S-1). For M-ZrO$_2$, the compressive strain increases with decreasing nanocrystal size; in contrast, for T-ZrO$_2$, the effective strain fluctuates around zero, indicating a relaxed strain state. For nanocrystals of the same size < 10 nm, M-ZrO$_2$ endures larger compressive strain than T-ZrO$_2$. The size-related difference $\Delta \eta$ contributes to the total energy of the material. Therefore, for the first time, this gives direct evidence that T-ZrO$_2$ can be more stable than M-ZrO$_2$ for limited crystallite sizes, as a result of strain–size concerns. This is consistent with the theoretically calculated critical value of 10 nm, and also with the value of 30 nm calculated in the case of polymorphs with interfacial energies counted. Since the compressive strain increased drastically when the nanocrystal size was < 5 nm for M-ZrO$_2$, this gives a convincing explanation for the fact that M-ZrO$_2$ nanocrystals with size < 2.8 nm cannot be synthesized. From another perspective, a high intrinsic compressive strain is indispensable for the stabilization of M-ZrO$_2$ nanocrystals with size < 10 nm. This is a likely reason why the martensitic transformation was not observed in our experiments.

The size-related effective strains can also be affected by doping. When the doping level was increased from 2% to 30%, the size of the Y:T-ZrO$_2$ nanocrystals decreased. The effective strain of 2%Y:T-ZrO$_2$ falls between the T-ZrO$_2$ and M-ZrO$_2$ gap, while 10% and 30%Y:T-ZrO$_2$ fit well within the pure T-ZrO$_2$ region. This indicates that doping with yttrium ions alleviates the compressive strain, and thus, yields the tetragonal phase.

2.7 Photoluminescence (PL) properties

The UV-vis absorption spectra of T-ZrO$_2$ and M-ZrO$_2$ nanocrystals are shown in Figs. 5(a) and 5(b). Since
bulk ZrO$_2$ of either monoclinic or tetragonal phase has a forbidden band of about 4.9–5.0 eV [53, 54], the observed peak within the range 4.8–5.2 eV can be identified as the band gap absorption.

Figures 5(c) and 5(d) show the PL spectra measured for ZrO$_2$ dispersed in cyclohexane. The spectra range from ultraviolet (300 nm) to the visible (600 nm). Although still somewhat controversial, it is generally accepted that for various oxide/sulfide nanomaterials, such as ZnS, ZnO, SnO$_2$, SiO$_2$, In$_2$O$_3$, and ZrO$_2$, the relatively broad PL spectra arise from emission of the oxygen or sulfur defect states [30, 44, 45, 55–58]. The PL intensity of the yttrium-doped ZrO$_2$ nanocrystals was stronger than undoped samples, indicating higher defect density. For T-ZrO$_2$, the PL spectrum peak shifted from 337 nm to 396 nm when the size increased from ~1 nm to ~3 nm. The PL spectrum of 2%Y:T-ZrO$_2$ with a size ~5 nm showed a further red-shift to 458 nm. For M-ZrO$_2$, the PL spectrum peak shifted from 402 nm to 442 nm when the size increased from ~4 nm to ~5 nm. Similar size-related PL properties have also been reported for the wide band semiconductors SnO$_2$ and ZnS as nanocrystals and as nanorods/ultrathin nanowires.
Figure 5 (a) Absorption spectra of T-ZrO₂ nanocrystals and ultrathin nanowires. (b) Absorption spectra of M-ZrO₂ nanocrystals. (c) PL spectra of T-ZrO₂. (d) PL spectra of M-ZrO₂ nanocrystals. (e) PL spectra of M-ZrO₂ nanocrystals (5–6 nm) with different excitation wavelengths. (f) and (g) Images of T-ZrO₂ and M-ZrO₂ nanocrystals, respectively, dispersed in cyclohexane and their fluorescence under 365 nm excitation.

[44, 57]. Figure 5(e) shows that by changing the excitation wavelength from 320 nm to 520 nm, the PL spectrum peak shifted accordingly. It was noticed that when the excitation wavelength exceeded 400 nm, the PL intensity decreased drastically.

3. Conclusions

M-ZrO₂ nanocrystals, pure and yttrium-doped T-ZrO₂ nanocrystals, and ultrathin T-ZrO₂ nanowires have been successfully synthesized using a solvothermal method. The nanocrystal size, morphology, and phase can be well controlled by tuning the reaction system and by doping. The effective compressive strain in the M-ZrO₂ nanocrystals increases with decreasing nanocrystal size. The difference in the strain-size diagrams of M-ZrO₂ and T-ZrO₂ gives direct evidence for the stability of T-ZrO₂ and M-ZrO₂ nanocrystals at room temperature. The controllability of the zirconia phases, morphologies, and sizes provides...
the basis for their surface and energy structure design. Therefore, tunable structural, semiconductor, and catalytic properties can be expected for such materials.

Acknowledgements

The authors thank the National Natural Science Foundation of China (Nos. 20725102 and 50772056), the Foundation for the Authors of National Excellent Doctoral Dissertation of China, the Program for New Century Excellent Talents of the Ministry of Education of China, the Fok Ying Tung Education Foundation (111012), and the State Key Project of Fundamental Research for Nanoscience and Nanotechnology (2006CB932301) for financial support.

Electronic Supplementary Material: Supplementary material is available in the online version of this article at http://dx.doi.org/10.1007/s12274-009-9092-x and is accessible free of charge. It contains the enlarged images of Figs. 1(b), 1(e), and 1(h), Figs. 2(b), 2(d), and 2(e), showing the microstructure details of the ZrO2 nanocrystals, and details of the calculations using XRD data to obtain nanocrystal size, effective strain, and error bars.

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