Supporting information

Modifying the phase and controlling the size of monodisperse ZrO_2 nanocrystals by employing Gd^{3+} as nucleation agent

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1. Experimental

Materials: $ZrOCl_2$, $GdCl_3$, oleic acid, sodium oleate (NaOA), NaOH, cyclohexane, ethanol and ammonia (15 wt%) were all purchased from Sinopharm Chemical Reagent Company. All chemicals were of analytical grade and used without further purification. Deionized water was used in the reaction.

Synthesis: In a typical synthesis, 10 ml aqueous solution of $ZrOCl_2$ (50 mol/L) was mixed with ethanol (10 mL), oleic acid (10 mL) and NaOA (0.8 g) under thorough stirring. Then, 1 mL ammonia (15 wt%) solution was added to the mixture. After vigorously stirring at room temperature for 10 min, the colloidal solution was transferred into a 25 mL Teflon-lined autoclave, sealed and heated at 200 ℃ for 24 h. The final products were collected, washed several times with ethanol/cyclohexane, and purified by centrifugation. To introduce Gd^{3+} into the reaction system, $GdCl_3$ with designed concentration (in mol%) was added.

Characterization: To study the phase structure of the products, X-ray diffraction

(XRD) analyses were carried out with a powder diffractometer (DMAX2500 RIGAKU) using Cu Kα radiation (λ=0.154 nm). The microstructure of the samples were observed by a transmission electron microscope (TEM, JEM-2010) equipped with an energy dispersive x-ray spectroscope (EDS). TEM specimens were prepared by directly drying a drop of a dilute cyclohexane dispersion solution of the products on the surface of a carbon-coated copper grid. The actual chemical compositions were determined by inductively coupled plasma (ICP) technique on a Perkin-Elmer Optima 3300DV spectrometer. The magnetization as a function of the applied magnetic field ranging from -100 to 100 kOe was measured using a Quantum Design PPMS-7 magnetometer. All the measurements were carried out at room temperature. UV absorption of the products dispersed in cyclohexane was measured by a Lambda 900 UV-vis spectrometer. Size distribution analysis was carried out by measuring the diameters of 200 particles.

2. Figure S1-S4

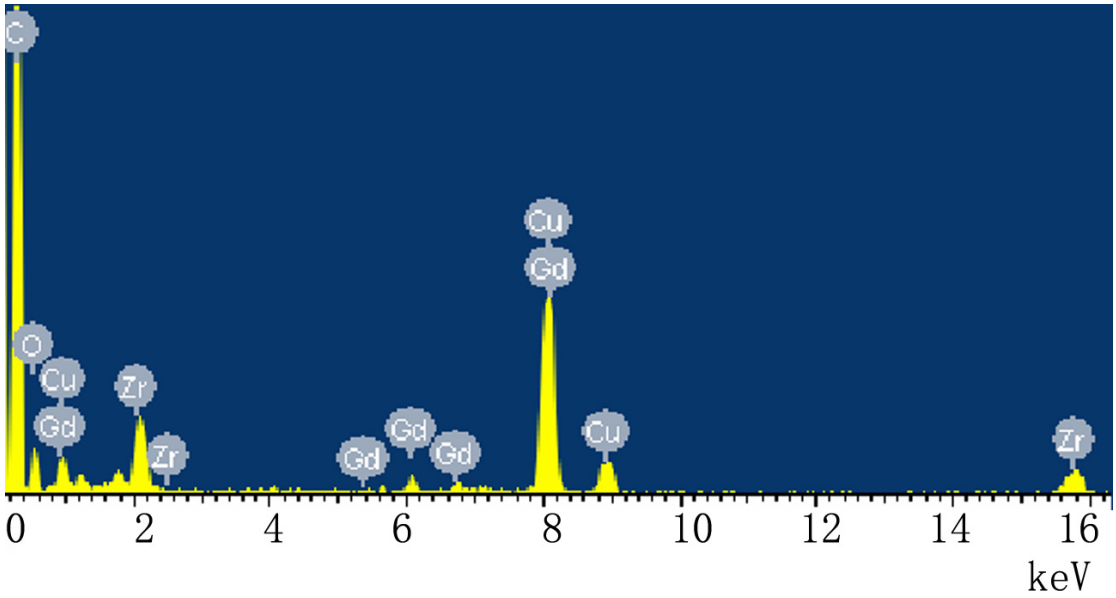

Figure S1. EDS spectrum taken from ZrO_2 nanocrystals synthesized with 5% Gd^{3+} addition, which demonstrates the presence of Gd^{3+} in ZrO_2 nanocrystals. The Cu and C signal come from the micro-grid.

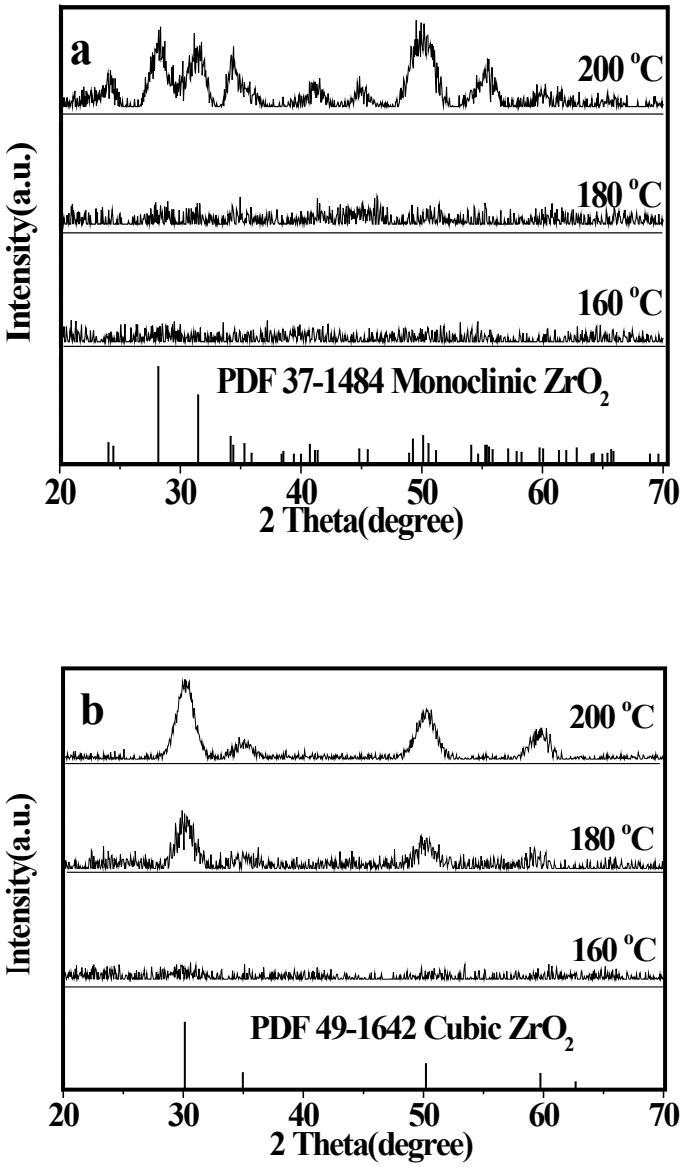

Figure S2. XRD patterns of ZrO_2 products synthesized at various temperatures for 24 h: (a) without Gd^{3+} addition, and (b) with 5% Gd^{3+} addition; bars at bottom of (a) and (b) represent the standard crystal data of monoclinic (PDF 37-1484) and cubic (PDF 49-1642) ZrO_2 respectively.

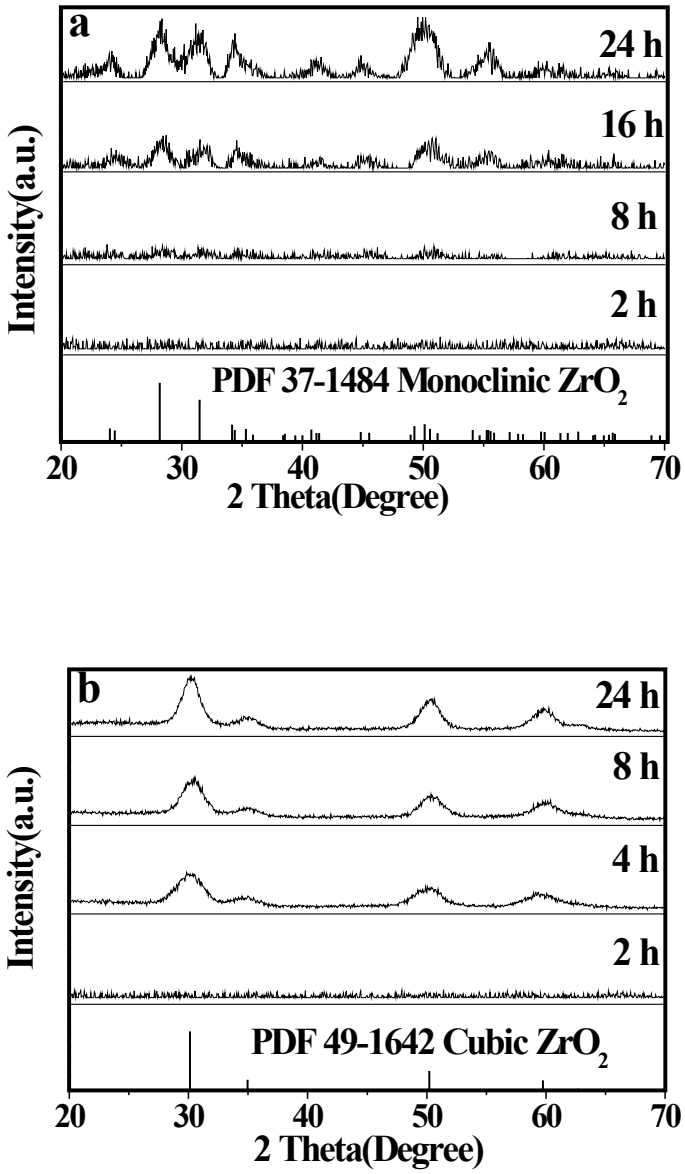

Figure S3. XRD patterns of ZrO_2 products synthesized at 200 ℃ for various durations: (a) without Gd^{3+} addition, and (b) with 5% Gd^{3+} addition; bars at bottom of (a) and (b) represent the standard crystal data of monoclinic (PDF 37-1484) and cubic (PDF 49-1642) ZrO_2 respectively.

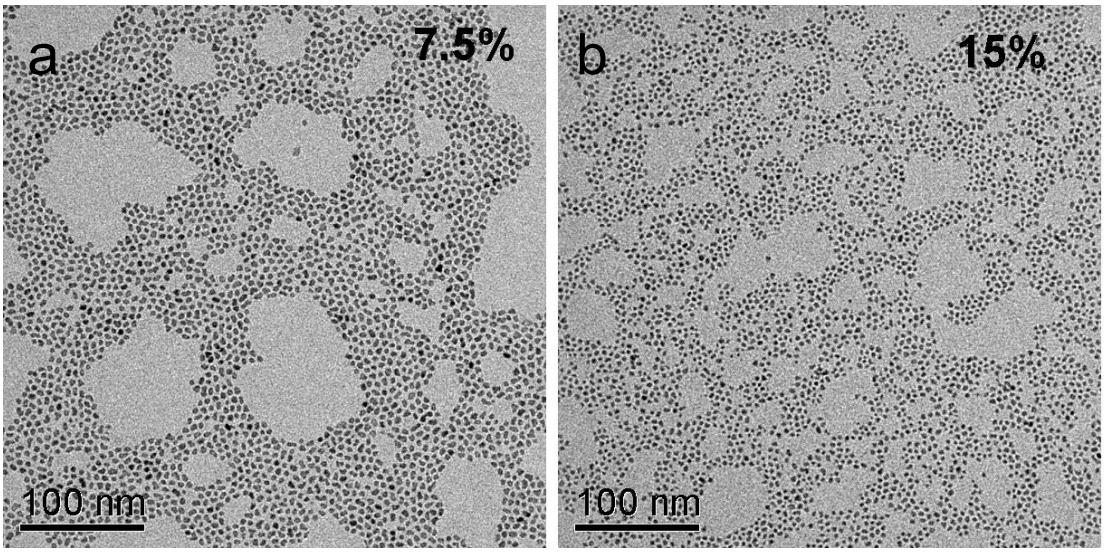

Figure S4. TEM micrographs of cubic ZrO_2 nanocrystals synthesized with (a) 7.5%, and (b) 15% Gd^{3+} addition.

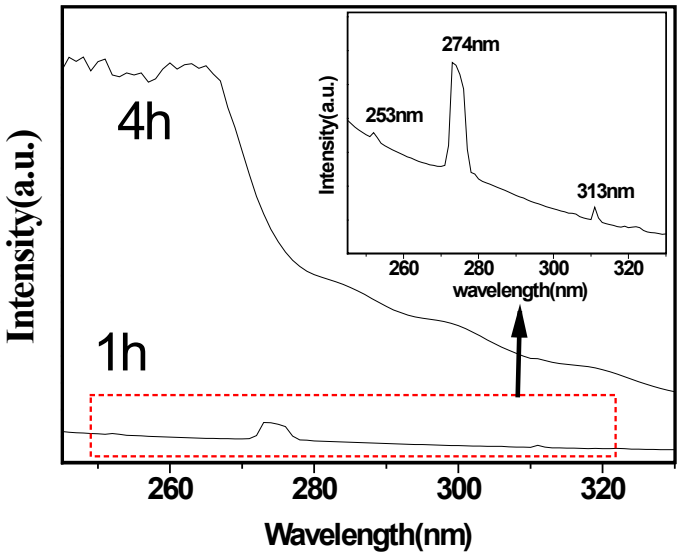

Figure S5. UV absorption spectra of the products having reacted for 1h and 4h in the solution system added with 10 mol% Gd^{3+}; inset is the magnified absorption spectrum of the product having reacted for 1h.

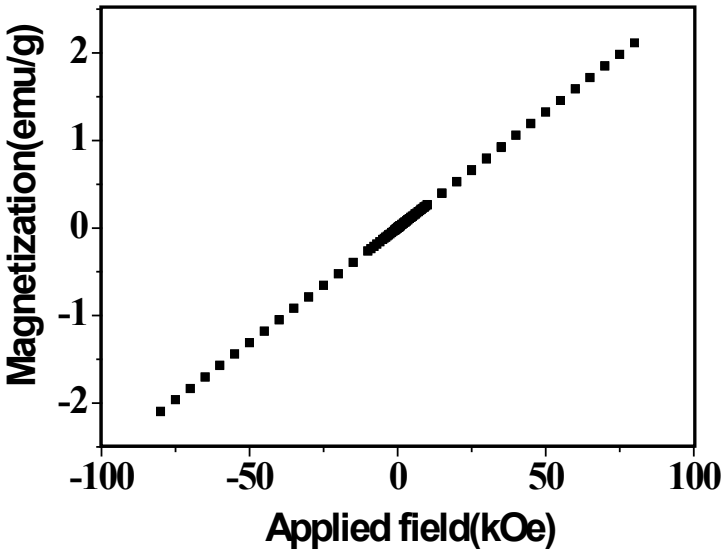

Figure S6. Room temperature magnetization as a function of applied field for cubic ZrO_2 nanocrystals with 20% Gd^{3+}.

3. Actual composition analysis

Table S1. Nominal and actual contents of Gd^{3+} in the synthesized ZrO_2 nanocrystals

	Nominal Gd^{3+} content (in mol%)	ICP measured actual Gd content (in mol%)
Sample 1	10%	9.4%
Sample 2	20%	18.6%