Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013

Supporting Information

The investigations on crystal plane effect of ceria on gold catalysis in the oxidative dehydrogenation of alcohols and amines in liquid phase

Min Wang, Feng Wang,* Jiping Ma, Mingrun Li, Zhe Zhang, Yehong Wang,
Xiaochen Zhang, Jie Xu*

Dalian National Laboratory for Clean Energy, State Key Laboratory of Catalysis

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023 (P.R. China)

*Corresponding author: E-mail: wangfeng@dicp.ac.cn, xujie@dicp.ac.cn

Content:

Experimental Section

Synthesis of ceria

CeO_2 nanorod, nanocubic and nanoparicles were prepared as reported. [1] Typically, $Ce(NO_3)_3$ (6 mmol) was added into a NaOH aqueous solution with appropriate concentration (120 mL, C_{NaOH}). This stock solution was stirred at room temperature for 10 min in a Teflon bottle and then sealed tightly in a stainless-steel autoclave. Hydrothermal treatment was carried out at different temperatures (T) for 24 h. After cooling, the white precipitates were collected, washed with deionized water, and dried at 80 ^oC. The dried yellow powders were calcined in air at 300 ^oC for 3 h. The values of C_{NaOH} and T were varied according to the target crystal shape (CeO_2 nanorod: C_{NaOH} = 6 M, T = 100 ^oC; CeO_2 nanocube: C_{NaOH} = 6 M, T = 180 ^oC; CeO_2 nanoparicles: C_{NaOH} = 0.1 M, T = 180 ^oC). CeO_2 nanooctahedra were prepared according to reported paper. [2] cerium(III) nitrate hexahydrate (3 mmol) trisodium phosphate hexahydrate (0.03 mmol) were dissolved in distilled water (120 mL). After being stirred at room temperature for 1 h, the mixed solution was transferred into Teflon-lined stainless autoclave and heated at 170 ^oC for 12 h.

Synthesis of Au/CeO_2

The deposition of Au onto the ceria substrate was conducted using deposition–precipitation (DP) method. In brief, the CeO_2 were dispersed in an aqueous solution of $HAuCl_4$ at a fixed pH of 10. The nominal Au loading was 1.0 wt%. The suspension was aged at room temperature for 24 h and washed with deionized water several times. The final Au containing material was obtained by calcination in air at 300 ^oC for 3 h. For brevity, gold supported on CeO_2 nanorod, nanoparticles, nancube and nano-octahedra were denoted as Au/CeO_2-R, Au/CeO_2-P, Au/CeO_2-C and Au/CeO_2-O, respectively. ICP analysis shows that the gold loading were 1.1 wt%, 1.2 wt%, 0.8 wt% and 0.9 wt% for Au/CeO_2-R, Au/CeO_2-P, Au/CeO_2-C and Au/CeO_2-O, respectively.

Oxidation of alcohols

1 mmol of alcohols, 0.05 mmol of p-xylene as internal standard, 5 mL chlorobenzene, catalyt (0.1 mol% Au) and magnetic stir were added to two-necked round bottom flask. O_2 were bubbled through a needle connected with a side-mouth sealed with Teflon septum. The reactor was placed into an oil bath which was thermally stabilized at the desired temperature. Aliquots were collected at intervals. The reactant and product were analyzed and quantified by gas chromatography−mass spectrometry (GC−MS) using an Agilent 7890A/5975C instrument equipped with an HP-5MS column (30 m in length, 0.25 mm in diameter). The conversion was determined using internal standard method. The selectivity was determined using area normalization method.

Hot filtration test

The benzyl alcohol oxidation mixture was quickly filtered through a Teflon-membrane filter after 1 h to another pre-heated glass reactor with Cs_2CO_3, which was placed in the same oil-bath with the previous one. The reaction was then conducted with the filtrate for another 8 hour. Four samples were collected at 3 h, 5 h, 7 h and 9 h, and analyzed.

Oxidation of amines

0.2 mmol of amines, 0.05 mmol of p-xylene as internal standard, 2 mL of 1,4-dioxane and catalyst (0.25 mol% Au) were added to stainless steel autoclave. After heating to the desired temperature, the oxygen was charged into the reactor to 0.3 MPa and the reaction was performed for 6 h under magnetic stirring. The reactant and product were analyzed and quantified by gas chromatography−mass spectrometry (GC−MS) using an Agilent 7890A/5975C instrument equipped with an HP-5MS column (30 m in length, 0.25 mm in diameter). The conversion was determined using internal standard method. The selectivity was determined using area normalization method.

Characterizations

The nitrogen sorption experiments were performed at 77 K on a Quantachrome Autosorb-1 system with micropore analysis. Prior to the measurement, the samples were outgassed at 150 ^{o}C. The Brunauer-Emmett-Teller (BET) specific surface areas were calculated using adsorption data at a relative pressure range of P/P_0: 0.05-0.25. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG ESCALAB MK2 spectrometer equipped with an AlK α X-ray source (hυ = 1486.6 eV) and operating at 12.5 kV and 220 W. The binding energy (BE) was calibrated with the C1s signal (285.0 eV) as a reference. Raman spectra were recorded on a micro-Raman spectrometer (Renishaw) equipped with a CCD detector using a He/Ne laser with a wavelength of 514 nm. Microstructures of the catalysts were examined by transmission electron microscopy (TEM, JEOL JEM-2000EX) and high resolution electron microscopy (HRTEM, FEI Tecnai G2 F30 S-Twin).

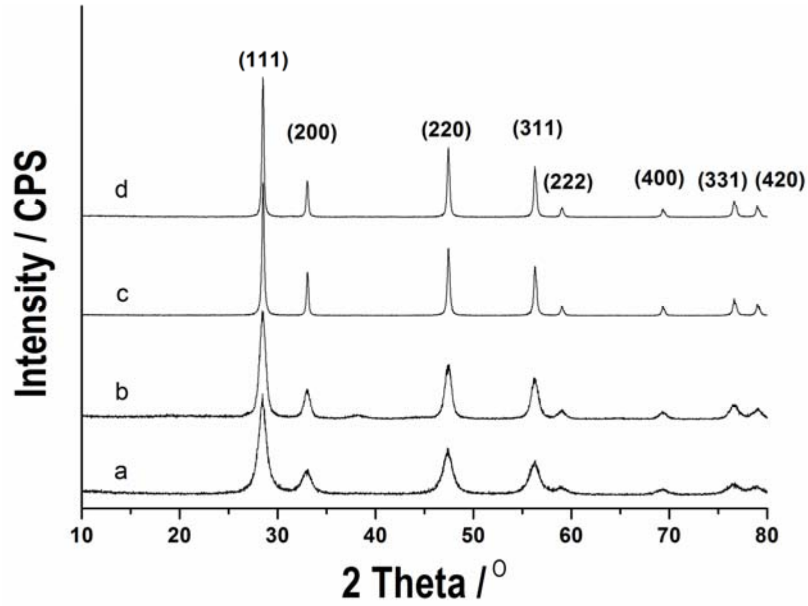

Fig. S1 XRD parttens of (a) Au/CeO$_2$-R, (b) Au/CeO$_2$-P, (c) Au-CeO$_2$-C and (d) Au/CeO$_2$-O.

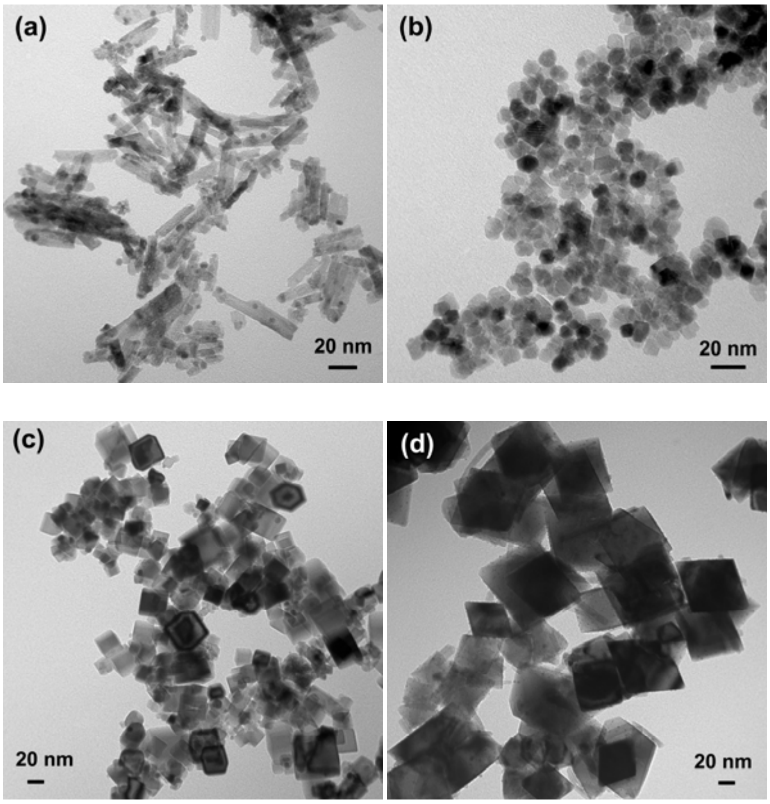

Fig. S2 TEM images of (a) Au/CeO_2-R, (b) Au/CeO_2-P, (c) Au/CeO_2-C and (d) Au/CeO_2-O.

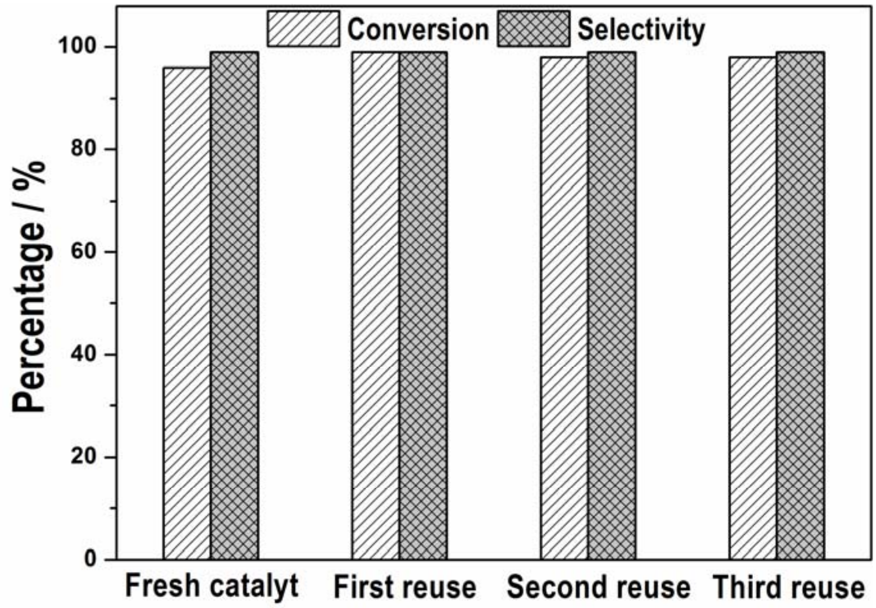

Fig. S3 Reuse of the Au/CeO_2-R in the benzyl alcohol oxidation. Reaction conditions: 1 mmol benzyl alcohol, 0.5 mmol p-xylene, 5 mL chlorobenzene, 20 mg catalyt, O_2 1atm, 90 ^oC, 8 h.

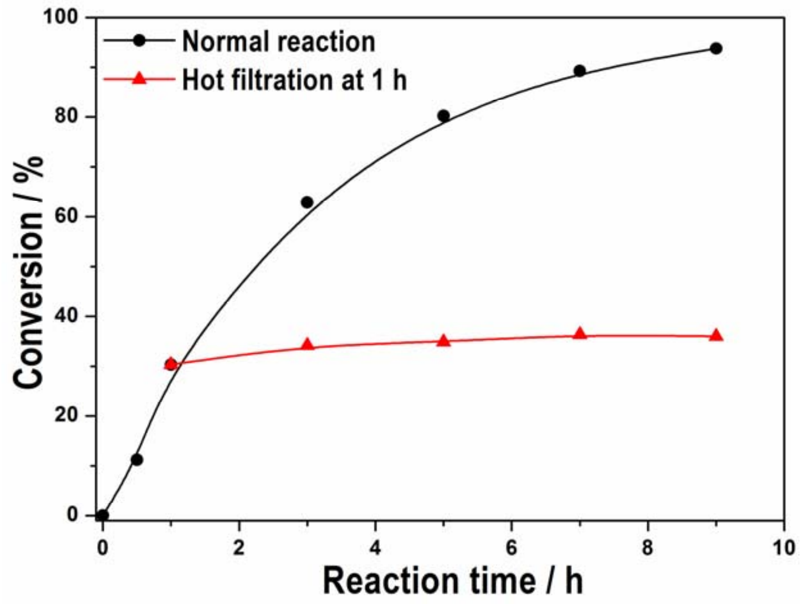

Fig. S4 Hot filtration experiment. Reaction conditions: 1 mmol benzyl alcohol, 0.5 mmol p-xylene, 5 mL chlorobenzene, 20 mg catalyt, O_2 1atm, 90 ^{o}C, 8 h. The catalyst was filtrated at 1 h.

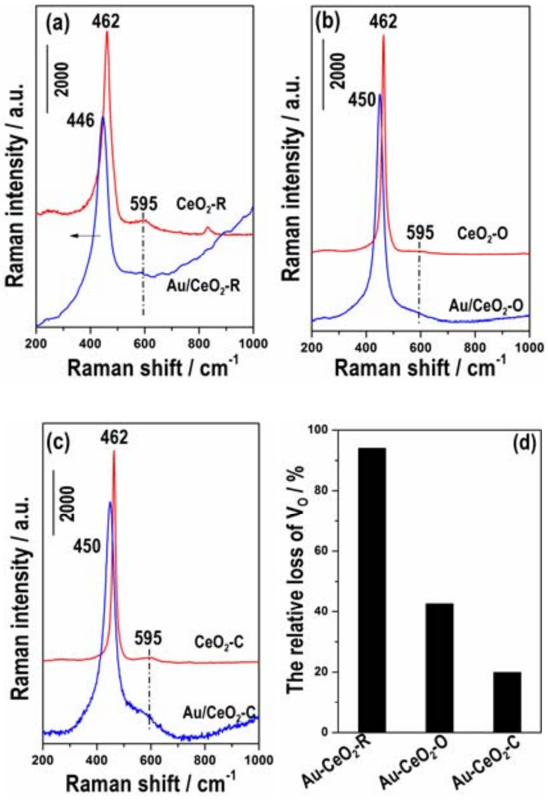

Fig. S5 Raman (514 nm) characterization of the VÖ in different crystal plane after gold deposit. (a) Au/CeO_2-R{110}, (b) Au/CeO_2-O{111} and (c) Au/CeO_2-C{100}; (d)The comparison of the loss of VÖ after gold deposit among three samples.

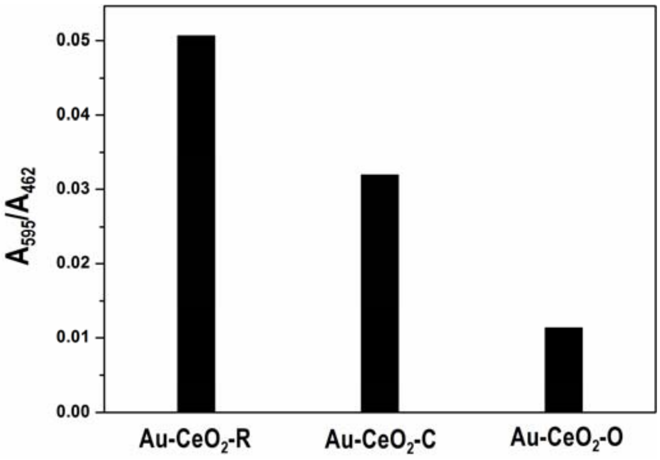

Fig. S6 The comparison of surface concentration of oxygen vacancy sites in different catalyst.

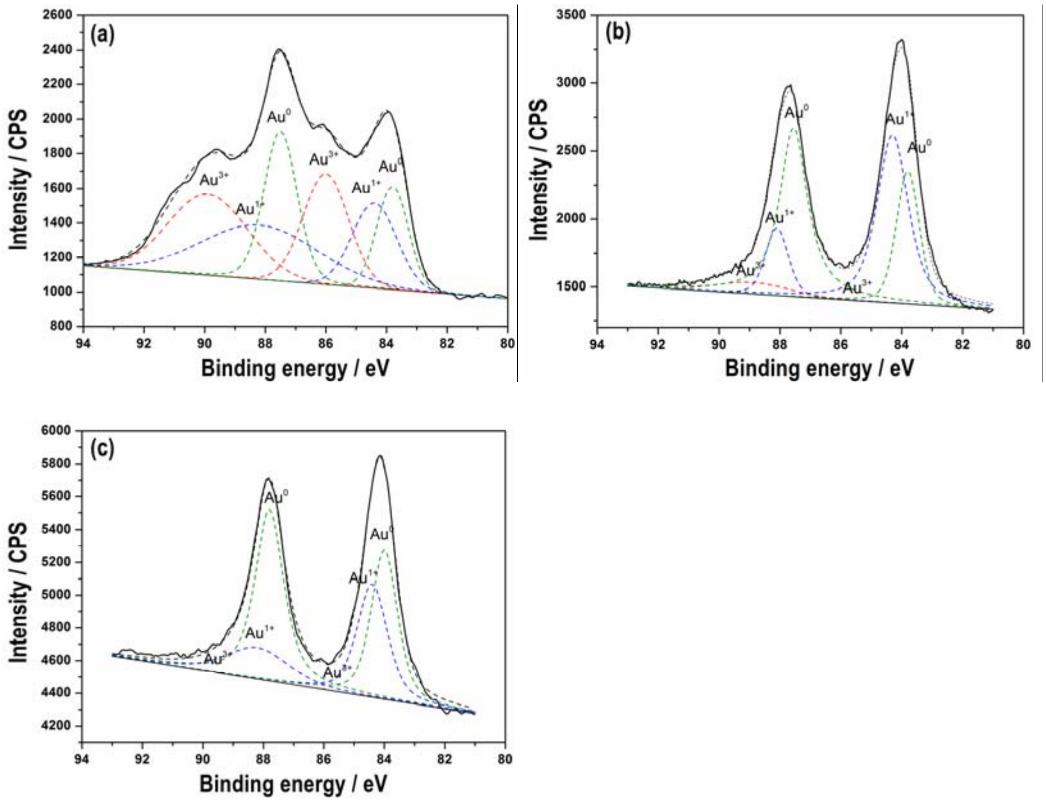

Fig. S7 XPS characterization of the gold species of (a) Au-CeO_2-R, (b) Au-CeO_2-O and (c) Au-CeO_2-C.

Table S1. Concentration of gold species in Au/CeO_2 samples determined by XPS

Catalyst	Au^0/Au_T	Au^+/ Au_T	Au^{3+}/ Au_T	$(Au^+ + Au^{3+})/ Au_T$
Au/CeO_2-R	28.3%	20.3%	51.4%	71.7%
Au/CeO_2-O	52.7%	43.1%	4.3%	47.3%
Au/CeO_2-C	63.5%	36.5%	-	36.5%

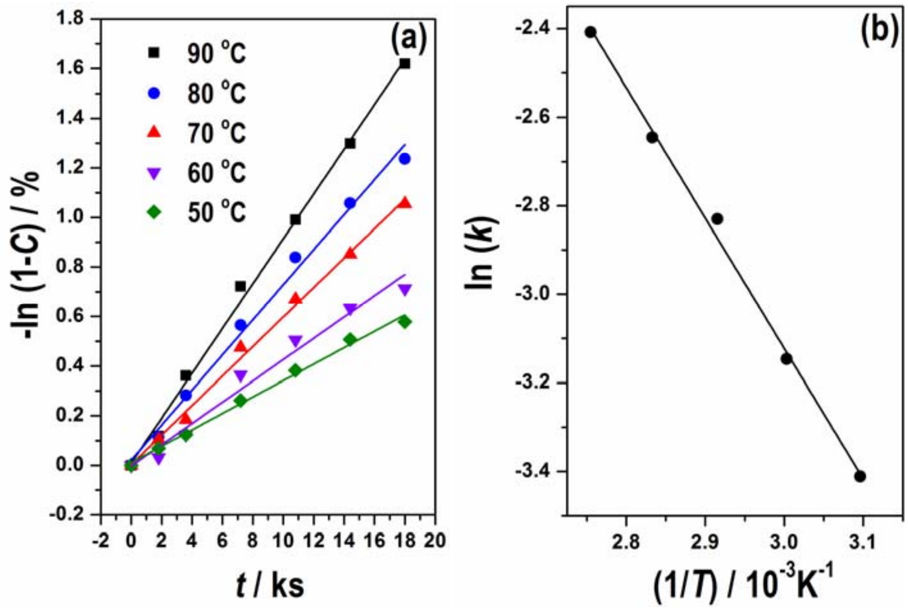

Fig. S8 (a) Kinetic analysis over the Au/CeO_2-R. (b) Arrhenius plot

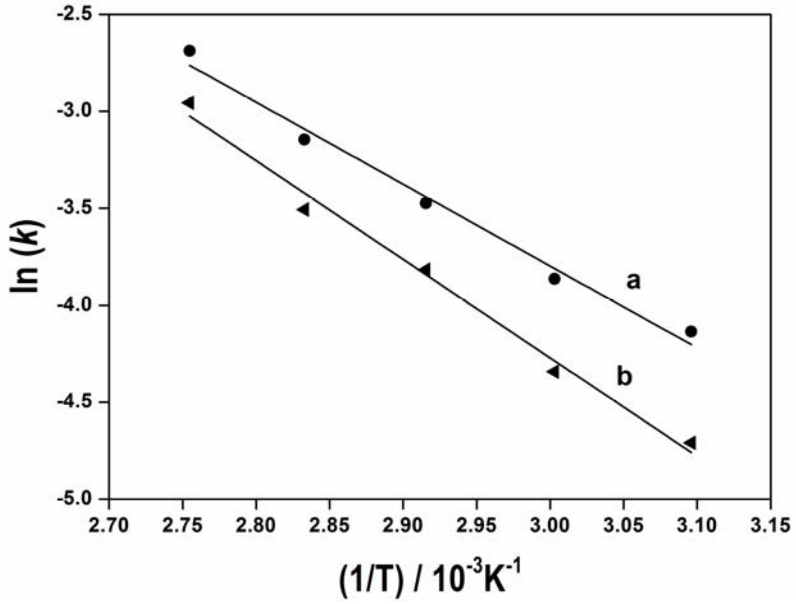

Fig. S9 Arrhenius plots for the oxidation of benzyl alcohols by (a) Au/CeO_2-P, *Ea* = 35.1 kJ mol^{-1} and (b) Au/CeO_2-O, *Ea* = 42.3 kJ mol^{-1}.

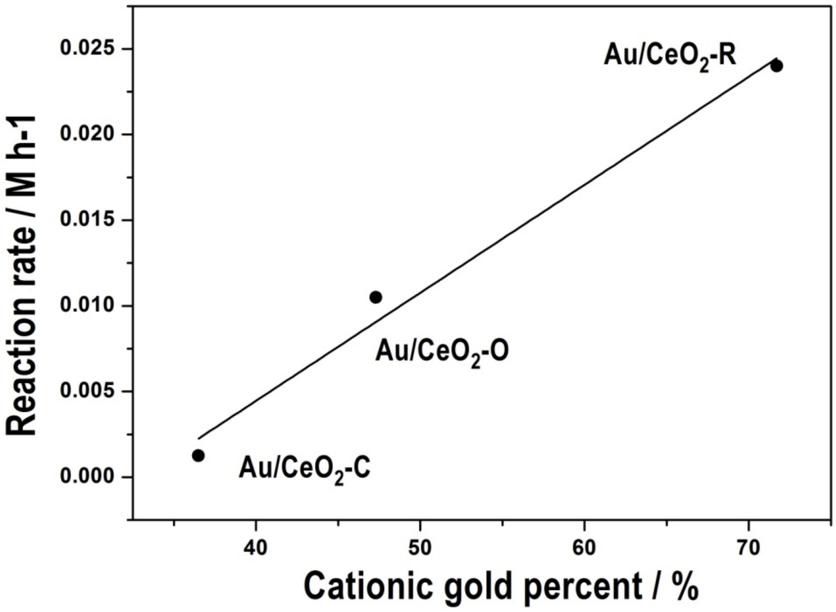

Fig. S10 Correlation between cationic gold percent and reaction rate for benzyl alcohol oxidation.

Reference:

[1] H. X. Mai, L. D. Sun, Y. W. Zhang, R. Si, W. Feng, H. P. Zhang, H. C. Liu, C. H. Yan, *J. Phys. Chem. B* 2005, **109**, 24380-24385.

[2] L. Yan, R. B. Yu, J. Chen, X. R. Xing, *Cryst. Growth. Des.* 2008, **8**, 1474-1477.