Supporting Information

Effect of Solvent on the Crystal Growth of One-Dimensional ZrO_2-TiO_2 Nanostructures

Rahima A. Lucky[1], Ruohong Sui,[2] John M. H. Lo,[2] and Paul A. Charpentier*[1]

[1]Department of Chemical and Biochemical Engineering,

University of Western Ontario, London, ON, Canada, N6A 5B9

[2] Presently at Department of Chemistry, the University of Calgary

2500 University Drive, NW, Calgary, AB, Canada, T1N 1N4

Table SI-1: Composition and weight loss at different stages of thermal analysis.

Solvent	Stage 1 25-120°C		Stage 2 120-260°C		Stage 3 260-500°C		Total wt% loss
	T_{p1}(°C)	Wt.(%)	T_{p2}(°C)	Wt.(%)	T_{p3}(°C)	Wt.(%)	
CO_2	40	6.02	200	20.68	343	18.97	45.72
Hexane	75	6.31	198	19.29	333	22.02	47.92
Xylenes	86	5.61	191	38.04	425	13.54	59.01
Isopropanol	95	4.55	236	42.95	319	8.88	57.59
Ethanol	53	10.07	196	14.11	336	22.5	49.34

Note-a- composition of as prepared nanomaterials.

Table SI-2. The thermodynamic properties and the average solubility parameters of the alkoxides.

Molecule	ΔH_f^{0} * (liquid) Kcal/mol	ΔH_f^{0} * (gas) Kcal/mol	ΔH_V^{0} * Kcal/mol	V^{0}(liquid) cm^3/mol	δ $(cal/cm^3)^{1/2}$
$Ti(OPr^i)_4$	-377**	-360**	17	296***	7.44
$Zr(OPr^i)_4$	-	-	31.5**	310***	9.99

Note: * ΔH_f^0, ΔH_V^0 and V^{0} denote the standard formation enthalpy, the enthalpy change of vaporization and the molar volume of the liquid, respectively.

** Ref. [26]

*** The molar volume was calculated from the density at 293 K. The liquid volume change was neglected for temperature changes from 293 to 298 K.

Table SI-3. The related atomic and group contributions to the energy of vaporization and mole volume at 25 °C.[33]

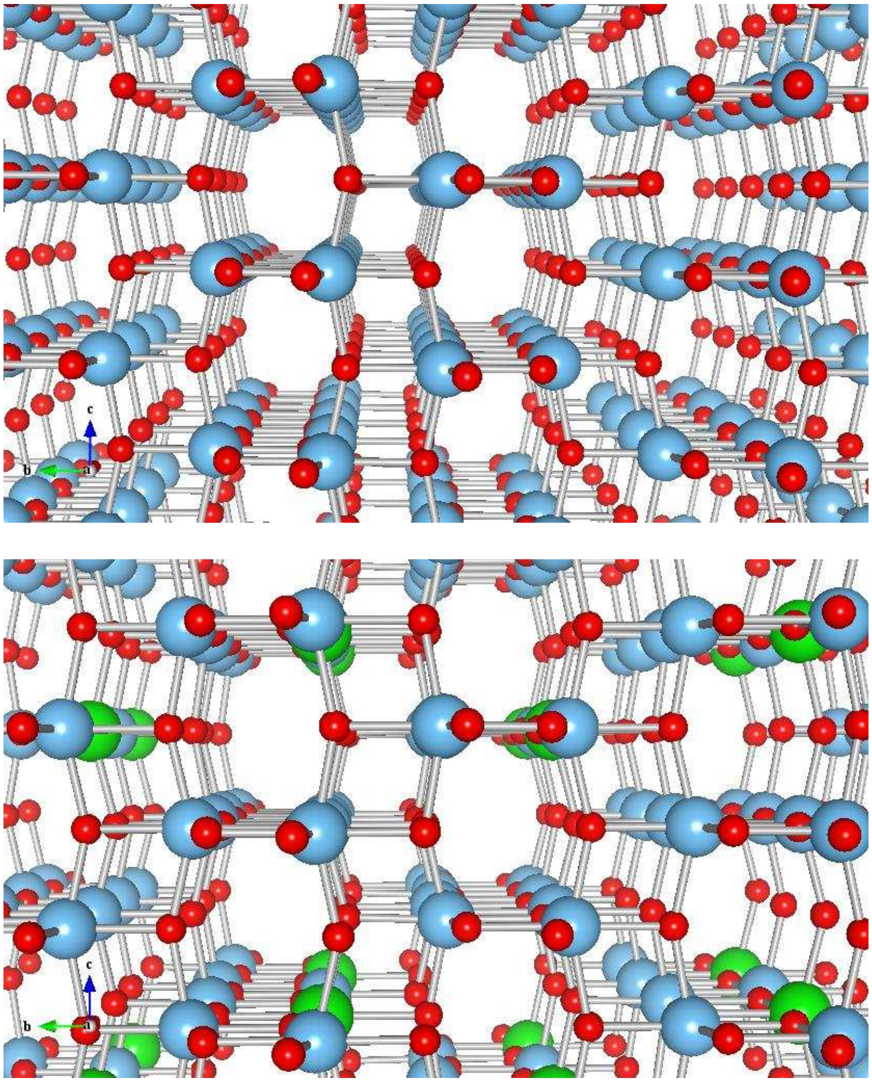
Atom or group	**Δe_i (cal/mol)**	**$\Delta \upsilon_i$ (cm^3/mol)**
CH_3	1125	33.5
CH	820	-1.0
COO	4300	18.0
O	800	3.8
Zr (calculated by this work)	15400	30.8
Ti (calculated by this work)	930	16.8

*- The solubility parameters of CO_2 are calculated for the selected temperature and pressure conditions using the density according to Giddings *et al.* with the provided values given in Table 2, [21]

$$\delta_{SC} = 1.25\sqrt{P_c}\,\frac{\rho_{R\,sc}}{\rho_{RL}} = 0.384\rho \qquad \text{(SI-1)}$$

where, P_c is the critical pressure in atmospheres, $\rho_{R\,sc}$ is the reduced density of CO_2, $\rho_{RL} = 2.66$ is the reduced density of liquid CO_2 at its normal boiling point, and ρ is the density of CO_2 in mol/L.

Figure SI-P1: The structures of DFT-optimized pure anatase (top) and Zr-doped anatase (bottom). Labels: Blue = Ti, Green = Zr, red = O.



Lattice parameters (in conventional definition of lattice axes of anatase; different from those shown in the figures)

(1x2x1) TiO_2: a = 3.80540 Å, b = 3.80549 Å, c = 9.47523 Å

(1x2x1) Zr-doped TiO_2: a = 3.83552 Å, b = 3.83017 Å, c = 9.59331 Å

(2x2x1) TiO_2: a = 3.80540 Å, b = 3.80549 Å, c = 9.47523 Å

(2x2x1) Zr-doped TiO_2: a = 3.83618 Å, b = 3.83510 Å, c = 9.62817 Å

The Zr-doped anatase unit cell was generated by replacing one Ti atom by a Zr atom for every two unit cells of TiO_2. This corresponds to the 12.5% of doping. In the (2x2x1) supercell, the two Zr atoms were placed such that the separation is farthest (the shortest Zr-Zr distance is 5.541 Å in the optimized (2x2x1) supercell of Zr-doped TiO_2); this can eliminate the local, artificial distortion of the unit cell symmetry due to the Zr dopants.

Details of the calculations of the (101) plane spacing of pure and Zr-doped anatase

The (101) plane spacing, d, can be deduced from the XRD spectrum using the Bragg's equation, d = (0.154 nm)/2 sin θ, where 0.154 nm is the wavelength of the X-ray source, and θ is the diffraction angle. For pure TiO_2 anatase, 2θ = 25.32 ^{o}, and thus d = 0.3513 nm. In this work, we observed that 2θ = 25.17 ^{o} for Zr-doped anatase, and this corresponds to d = 0.3535 nm. Hence, the percentage change in d is [(0.3535-0.3513)/0.3513] x 100% = 0.63%.

By trigonometry, we can derive the (101) plane spacing of anatase (in Å) in terms of lattice constants:

$$d = |c| \sin\left(\tan^{-1}\left(\frac{|a|}{|c|} \right) \right) \qquad \text{(SI-2)}$$

Using the parameters given in figure SIP1, we can calculate the spacing for (1x2x1) TiO_2:

$$d = 9.47523 \sin\left(\tan^{-1}\left(\frac{3.80540}{9.47523} \right) \right) = 3.5313 \text{ Å}$$

and for (1x2x1) Zr-doped TiO_2.

$$d = 0.95331 \sin\left(\tan^{-1}\left(\frac{3.83552}{9.59331} \right) \right) = 3.5571 \text{ Å}$$

The resulting change in d is thus [(3.5571-3.5313)/3.5313]x 100% = 0.73%. Similarly, we can calculate the d values for (2x2x1) pure anatase (d = 3.5313 Å), Zr-doped anatase (d = 3.5628 Å) and the corresponding deviation in d (%Δd = 0.89%).