Supporting information for

Doping Mechanism of Zn^{2+} ions in Zn-Doped TiO₂ Prepared by Sol-Gel Method

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Figure S1. XPS Ti2p (A) and O1s (B) spectra of P-500, Z-500-5, Z-500-30, P-800, Z-800-5 and Z-800-30. XPS depth profile of Zn 2p (C), Cl 2p (D) for Z-500-5 and Zn 2p (E) for Z-800-5.

To further demonstrate the existing states of surface O-Zn-Cl species and ZnTiO₃, XPS Ti2p and O1s spectra of different samples are plotted in Figure 3A and B respectively. In Figure S1A, the peaks of Ti2p for Z-500-5 shift to higher binding energy compared with P-500, caused by the formation of surface Ti-O-Zn-Cl species. As the electronegativity of Zn (1.6) is larger than that of Ti (1.5), an increase of the binding energies of Ti2p is observable. Moreover, the broader peak of Ti 2p for Z - 500-30 could be fitted into two new double peaks. Besides the Ti $2p_{3/2}$ peak of TiO₂(458.9 eV), the Ti $2p_{3/2}$ peak at 459.4 eV is attributed to that of ZnTiO₃¹. For Z-800-5 and Z-800-30 samples, the Ti $2p_{3/2}$ peaks belong to ZnTiO₃ species (459.4 eV) are also found. In comparison with Z-800-5, the peak intensity of Ti $2p_{3/2}$ ascribed to ZnTiO₃ for Z-800-30 increases, indicating the more and more Zn²⁺ ions form the ZnTiO₃ species with the increase of Zn content. It is found that the peak of Ti $2p_{3/2}$ for Z-800-X does not shift to higher binding energy compared with P-800 as no Ti-O-Zn-Cl species formed on the surface of TiO₂.

Similar results are also observed for O1s spectra. For P-500 sample shown in Figure S1B, the O1s spectrum could be deconvoluted into two peaks, ascribed to the lattice O (529.9 eV)in TiO₂ and surface oxygen (531.7 eV; such as surface bridge oxygen and hydroxy oxygen). In Zn doped TiO₂, the peak at 530.7 eV is attributed to lattice O of ZnTiO₃.



Figure S2. Raman Spectra of Z-500-x (A) and Z-800-x (B)

FigureS2 shows Raman Spectra of Z-500-x (FigureS1A) and Z-800-x (FigureS1B) samples. In FigureS1A, the Raman bands at 144cm⁻¹ (Eg), 196cm⁻¹(Eg), 396cm⁻¹ (B1g), 516cm⁻¹ (A1g and B1g), and 638cm⁻¹ (Eg) are observed for samples of P-500, Z-500-5 and Z-500-10, indicating an anatase structure for these samples.² Besides, one more peak at about 445cm⁻¹ can be observed for Z-500-10, which is attributed to formation of small amount of rutile structure in the sample.³ When the doping content of Zn is up to 20%, no narrow scattering bands can be observed in the Raman spectra due to the volatile products formed during the annealing process in the samples.

However, some weak wide peaks related to anatase and ZnTiO₃ can be observed for samples of Z-500-20 and Z-500-30. It suggests that the reaction of the doped Zn with TiO₂ occurs in the samples but the crystallization of the production ZnTiO₃ is not completely at the temperature of 500°C. In Figure S1B, all samples were annealed at temperature of 800°C. For P-800, the featured Raman peaks of rutile structure can be observed at143cm⁻¹(B1g), 236cm⁻¹(2 phonon process), 447cm⁻¹(Eg) and 612cm⁻¹(A1g).³ For the Zn-doped samples, besides the peaks of rutile, more narrow peaks observed at about 176cm⁻¹, 230cm⁻¹, 266cm⁻¹, 345cm⁻¹ and 708cm⁻¹, which indicates the crystalline phase of ZnTiO₃.^{1, 4-5} And with the increasing of doping content of Zn²⁺ ions, the intensity and the width of these Raman peaks become increased and narrowed respectively, suggesting the amount of ZnTiO₃ increased and the crystallinity improved, respectively.



Figure S3. Raman Spectra of Z-T-10 samples.



Figure S4. XRD patterns of TiO₂, 10%ZnTiO₃/TiO₂, Z-450-10 and 10%Rutile/Z-450-10.

We have prepared a series of TiO₂ based samples. 10%ZnTiO₃/TiO₂ is prepared with the same procedure with pure TiO₂(P-450), just with the addition of ZnTiO₃ powders. 10%Rutile/Z-450-10 is prepared by adding 10% molar fraction of Rutile. All samples exhibit typical anatase structure. For 10%ZnTiO₃/TiO₂ sample, besides the diffraction peaks of anatase, two small peaks at about 27.4° and 32.8° are observed, indicating the existence of rutile and ZnTiO₃. No peaks related to rutile is found for the pure TiO₂(P-450). Hence this further demonstrates that the existence of ZnTiO₃ is benefit for the phase transition from anatase to rutile. Moreover, in comparison with Z-450-10, there is no XRD peaks corresponding to ZnTiO₃ found for 10%Rutile/Z-450-10. Therefore the assumption that phase transition from rutile to anatase would promote the formation of ZnTiO₃ can be excluded.

sample	cell parameters (Å)			Cell volume	Crystal size	$d_{(hkl)}$ value (Å)			
	anatase	rutile	ZnTiO ₃	(Å ³)	(nm)				
P-500	a=b=3.785,	-	-	136.41	16.5±0.2	d ₍₁₀₁₎ =3.520			
	c=9.520								
Z-500-5	a=b=3.790,	-	-	136.83	14.8±0.2	d ₍₁₀₁₎ =3.529			
	c=9.525								
Z-500-10	a=b=3.811,	a=b=4.604,	-	137.21(A)	9.7±0.2 (A)	d ₍₁₀₁₎ =3.528			
	c=9.448	c=2.965		62.84(R)	32.6±0.2 (R)	d ₍₁₁₀₎ =3.256			
Z-500-20	-	a=b=4.598,	a=b=5.083,	62.57(R)	33.0±0.2 (R)	d ₍₁₁₀₎ =3.253			
		c=2.960	c=13.861	310.15(ZT)	30.6±0.2 (ZT)	d ₍₁₀₄₎ =2.733			
Z-500-30	-	a=b=4.600,	a=b=5.087,	62.68(R)	36.4±0.2 (R)	d ₍₁₁₀₎ =3.257			
		c=2.962	c=13.884	311.13(ZT)	30.4±0.2 (ZT)	d ₍₁₀₄₎ =2.736			

Table S1. Crystallite Size and Lattice Parameters of P-500 and Z-500-x samples(5≤x≤30).

Table S2. Crystallite Size and Lattice Parametters of P-800 and Z-800-x samples(5≤x≤30).

sample	cell parameters (Å)		Cell volume	Crystal size	d _(hkl) value (Å)
	Rutile	ZnTiO ₃	(Å ³)	(nm)	
P-800	a=b=4.594,		62.5	51.8±0.2	d ₍₁₁₀₎ =3.251
	c=2.961				
Z-800-5	a=b=4.596	a=b=5.026	62.57(R)	47.3±0.2 (R)	d ₍₁₁₀₎ =3.253
	c= 2.962	c=13.982	305.85(ZT)	47.3±0.2 (ZT)	d ₍₁₀₄₎ =2.735
Z-800-10	a=b=4.592	a=b=5.074	62.4(R)	42.3±0.2 (R)	d ₍₁₁₀₎ =3.246
	c= 2.959	c=13.977	311.68(ZT)	48.2±0.2 (ZT)	d ₍₁₀₄₎ =2.730
Z-800-20	a=b=4.595	a=b=5.025	62.52(R)	46.2±0.2 (R)	d ₍₁₁₀₎ =3.250
	c= 2.961	c=13.977	305.67(ZT)	49.3±0.2 (ZT)	d ₍₁₀₄₎ =2.732
Z-800-30	a=b=4.594	a=b=5.079	62.46(R)	46.2±0.2 (R)	d ₍₁₁₀₎ =3.249
	c= 2.960	c=13.928	311.17(ZT)	51.2±0.2 (ZT)	$d_{(104)}=2.731$

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