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Electronic Supporting Information

Synthesis and Antimicrobial Activity of ZnTi-Layered Double Hydroxide Nanosheets

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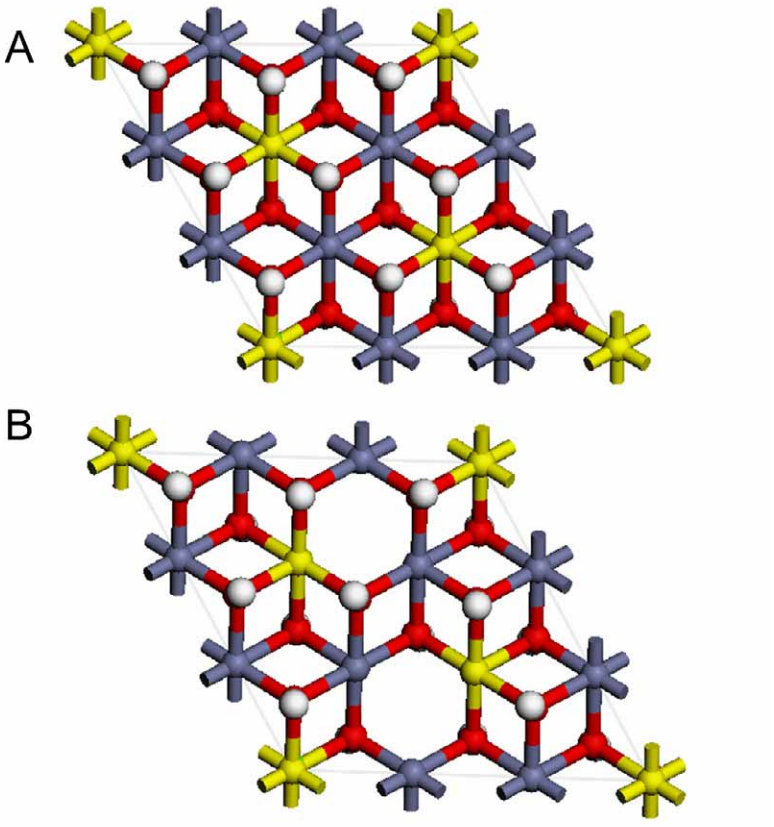
1. Computational details for electronic structure calculation

Plane-wave density functional theory (DFT) calculations for the electron band structure of $Zn_2Ti(OH)_6(CO_3)_{1/2}$ bulk and nano-sized LDH with Ti^{3+} active site were carried out using Dmol3 module in Material Studio 5.5 software package (Accelrys Inc.: San, Diego, CA).[1a] The 3×3×1 supercell (Scheme S1) was adopted for the LDH material as initial structure with lattice parameters $\alpha = \beta = 90°$, $\gamma = 120°$, a = b = 3.1 Å, which are in accordance with reported values. The parameter c was referred to the experimental data of this work (d = 7.76 Å for $Zn_2Ti(OH)_6(CO_3)_{1/2}$ bulk , and 31.08 Å for $Zn_2Ti(OH)_6$DDS). The generalized gradient approximation (GGA)[1b] with Perdew-Burke-Ernzerhof (PBE)[1c] functional was employed for the DFT exchange correlation energy, and 340 eV of cutoff was assigned to the plane-wave basis set. The self-consistent field (SCF) tolerance was 1×10^{-6} eV. The Brillouin zone was sampled by 1×1×1 k-points. The core electrons were replaced with ultrasoft pseudo-potentials.[1d] Scissors = 0.1 Ha.



Scheme S1. The supercell model for (A) ZnTi-LDH layer with 3×3×1 rhombohedral lattice (Yellow: Ti; Gray: Zn; Red: O; White: H); (B) ZnTi-LDH layer with Ti^{3+} defect (Yellow: Ti; Gray: Zn; Red: O; White: H).

2. Characterization Details

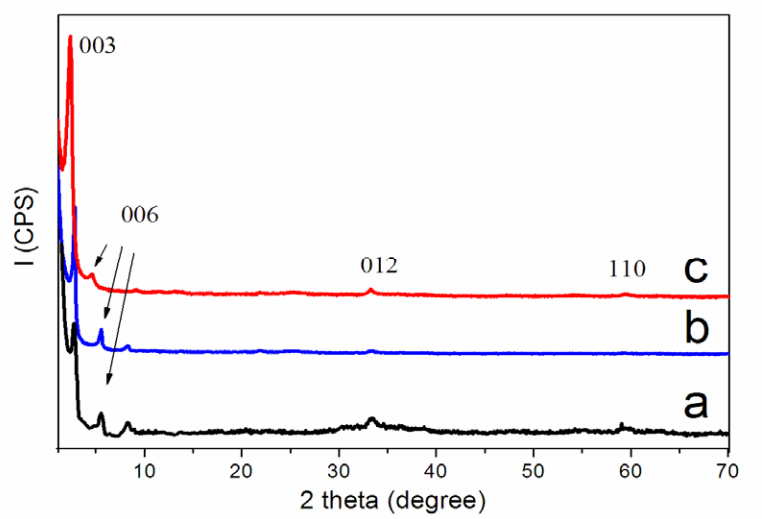


Figure S1 XRD patterns of (a) ZnTi-LDH-RM1, (b) ZnTi-LDH-RM2, (c) ZnTi-LDH-RM3.

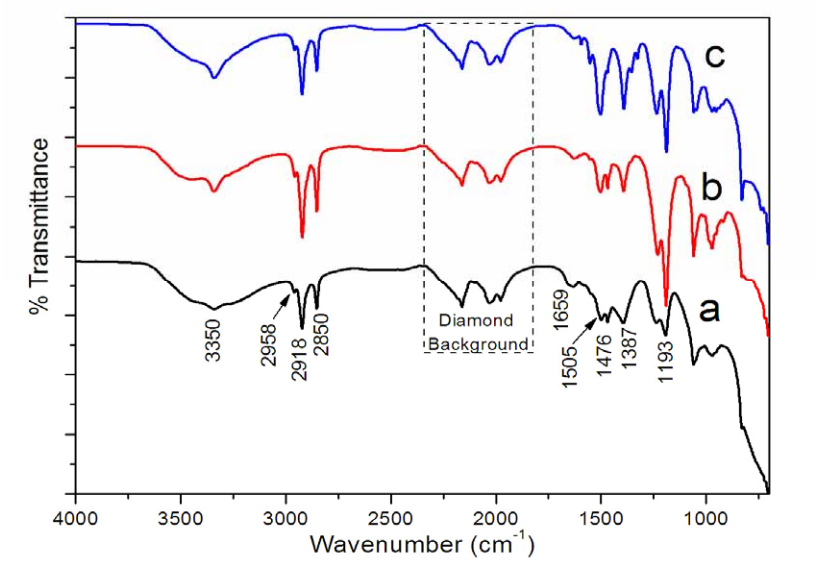


Figure S2 FT-IR spectra of (a) ZnTi-LDH-RM1, (b) ZnTi-LDH-RM2, (c) ZnTi-LDH-RM3.

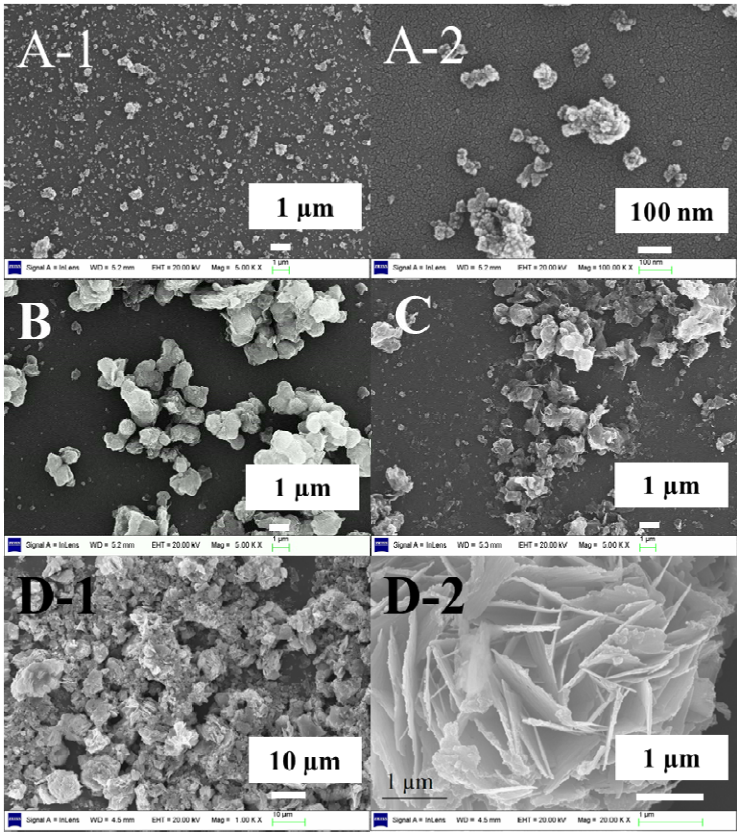


Figure S3 SEM images of ZnTi-LDH-RM1 at (A-1) low magnification and (A-2) high magnification; ZnTi-LDH-RM2 (B) and ZnTi-LDH-RM3 (C) at low magnification; the ZnTi-LDH-Bulk at (D-1) low magnification and (D-2) high magnification.

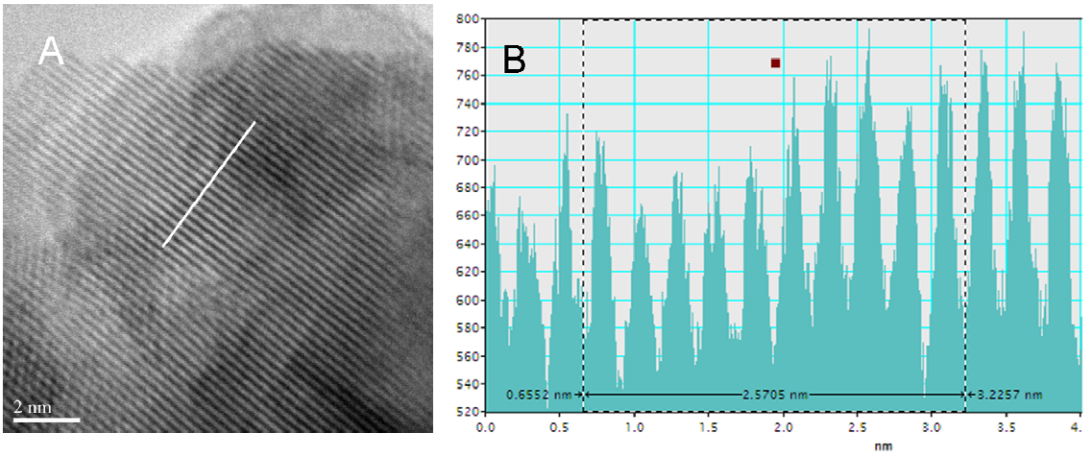


Figure S4 HRTEM images of ZnTi-LDH-Bulk at (A) high magnification, (B) line profile perpendicular to the *c*-axis along with the white line in A.

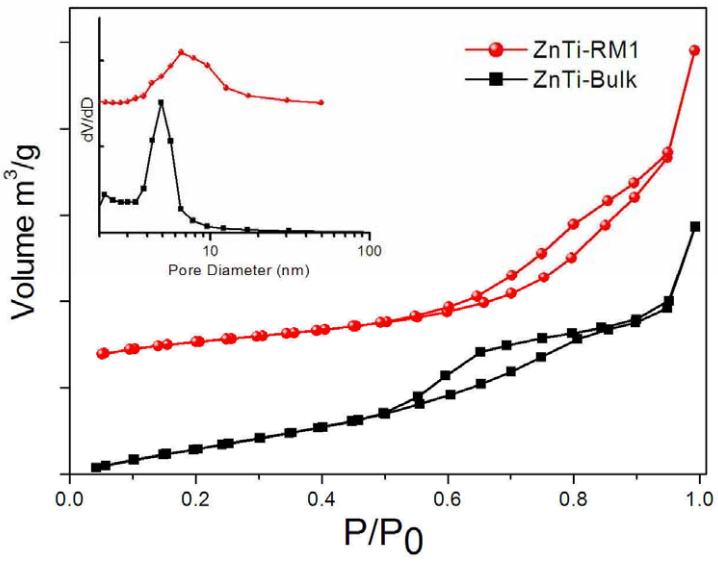


Figure S5 N_2-sorption isotherms and pore size distribution (inset) of ZnTi-LDH-RM1 and ZnTi-LDH-Bulk.

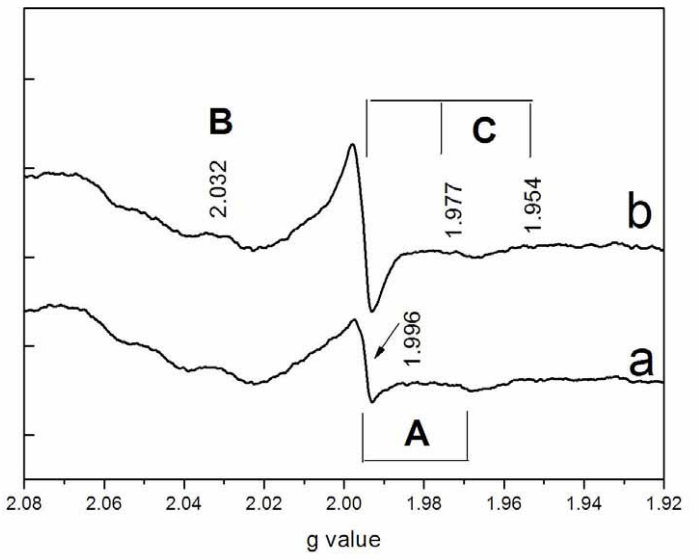


Figure S6 ESR spectra of (a) fresh ZnTi-LDH-RM1 and (b) after 20 min of visible light exposure at 110 K under N_2 atmosphere.

Table S1. The quantitative analyses of Ti^{4+} and Ti^{3+} in Ti 2p of ZnTi-LDH-RM1, ZnTi-LDH-Bulk, $K_2Ti_4O_9$ and rutile TiO_2 based on the results of XPS

Sample	Name	Energy/ eV	Area	Ti % (molar percentage)	Ti^{3+} % (molar percentage)
ZnTi-LDH-RM1	Ti^{4+} $2p_{3/2}$	458.5	17824	46.9	27.0
	Ti^{4+} $2p_{1/2}$	464.1	10118	26.6	
	Ti^{3+} $2p_{3/2}$	457.9	3267	8.6	
	Ti^{3+} $2p_{1/2}$	461.0	6764	17.8	
ZnTi-LDH-Bulk	Ti^{4+} $2p_{3/2}$	457.7	12016	59.3	14.7
	Ti^{4+} $2p_{1/2}$	463.2	5277	26.0	
	Ti^{3+} $2p_{3/2}$	456.9	1256	6.2	
	Ti^{3+} $2p_{1/2}$	460.0	1722	8.5	
$K_2Ti_4O_9$	Ti^{4+} $2p_{3/2}$	457.8	50690	67.8	0
	Ti^{4+} $2p_{1/2}$	463.5	24087	32.2	
	Ti^{3+} $2p_{3/2}$	—	—	—	
	Ti^{3+} $2p_{1/2}$	—	—	—	
Rutile TiO_2	Ti^{4+} $2p_{3/2}$	458.8	69512	66.6	0
	Ti^{4+} $2p_{1/2}$	464.5	35010	33.5	
	Ti^{3+} $2p_{3/2}$	—	—	—	
	Ti^{3+} $2p_{1/2}$	—	—	—	

Figure S7 shows the Fourier transform Zn curve fitting of *R*-space. The first shell of the Beta-$Zn(OH)_2$ represents the nearest-neighbor Zn–O coordination sphere with an average distance of ~1.97 Å and coordination number of 6.00. The second shell shows the Zn–Zn coordination sphere. The FT spectra of the ZnTi-LDH materials displays a great change of Ti local geometry. The second shell in the FT spectrum of ZnTi-LDH-Bulk (Figure S7, curve b), with a distance of ~3.24 Å and coordination number of 0.91, can be assigned to the Zn–Ti bond in LDH layer. The ZnTi-LDH-RM1 exhibits the shortest value of Zn–Ti bond (3.22 Å) and the lowest coordination number (0.64). The results indicate that Ti in ZnTi-LDH-RM1 sample undergoes a larger structural distortion compared with that of ZnTi-LDH-Bulk.

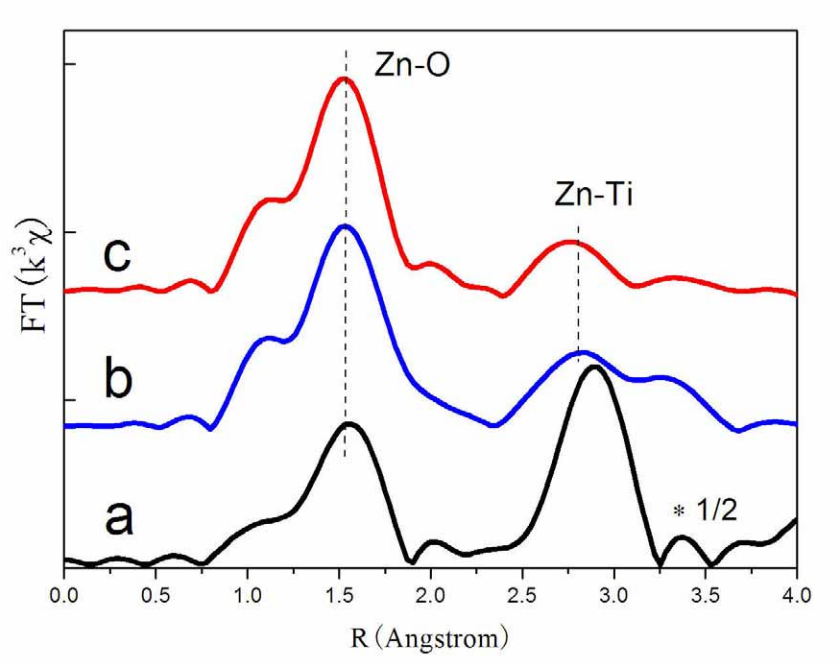


Figure S7 Magnitude of *k*2-weighted Fourier transforms of Zn K-edge EXAFS spectra for (a) Beta-$Zn(OH)_2$, (b) ZnTi-LDH-Bulk, (c) ZnTi-LDH-RM1.

Table S2. Local structure parameters around Zn in ZnTi-LDH estimated by EXAFS analysis

Sample	Shell	N[a]	R [Å][b]	σ^2 [Å^2][c]	ΔE_0 [eV][d]
Beta-$Zn(OH)_2$	Zn–O	6.00[e]	1.97	0.0066	2.00
	Zn–Zn	3.00	3.21	0.0050	1.00
ZnTi-LDH-Bulk	Zn–O	5.47	2.00	0.0075	–0.20
	Zn–Ti	0.91	3.24	0.0075	7.73
ZnTi-LDH-RM1	Zn–O	5.71	1.98	0.0075	–1.00
	Zn–Ti	0.64	3.22	0.0070	1.20

[a] N=coordination number; [b] R = distance between absorber and backscatter atoms; [c] σ^2 = Debye–Waller factor; [d] ΔE_0 = energy shift; R-space fit, Δr = –0.06–0.15 Å; [e] Fixed to 6 for the first hydroxide shell.

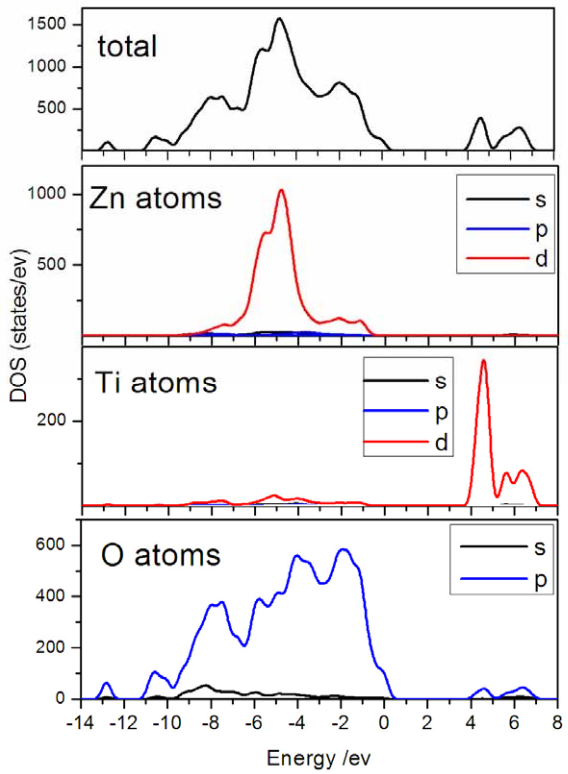


Figure S8 The total and partial density of states for the ZnTi-LDH-Bulk.

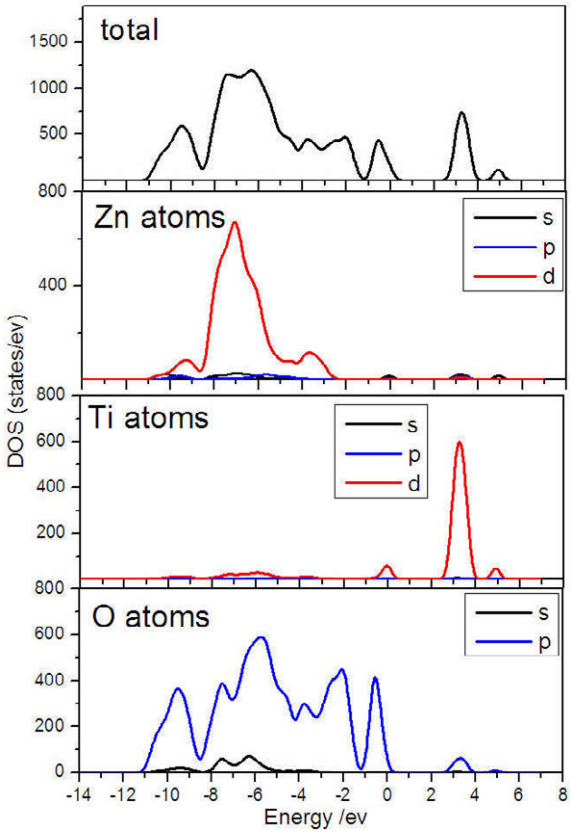


Figure S9 The total and partial density of states for the ZnTi-LDH with Ti^{3+}.

References:

[1] a) M. D. Segall, P. J. D. Lindan, M. J. Probert, J. Pickard, P. J. Hasnip, S. J. Clark and M. C. Payne, *J. Phys. Condens. Matter* 2002, **14**, 2717; b) J. A. White and D. M. Bird, *Phys. Rev. B* 1990, **41**, 7892; c) J. P. Perdew, K. Bruke and M. Ernzerhof, *Phys*. *Rev*. *Lett.* 1996, **77**, 3865; d) D. Vanderbit, *Phys. Rev. B* 1990, **41**, 7892.