

Electronic Supplementary Information

Zinc Titanium Glycolate Acetate Hydrate and its Transformation to

Zinc Titanate Microrods : Synthesis, Characterization and

Photocatalytic Properties

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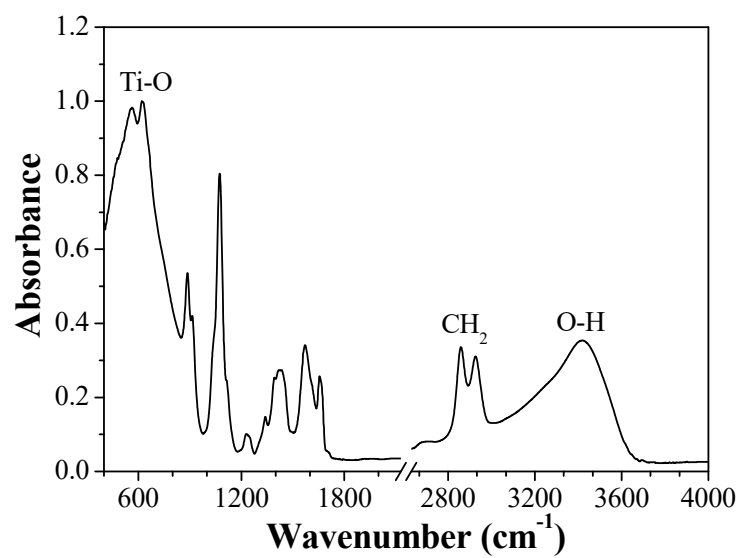


Fig. S1 FTIR spectrum of zinc titanium glycolate acetate hydrate (Zn₂Ti₃-GAH).

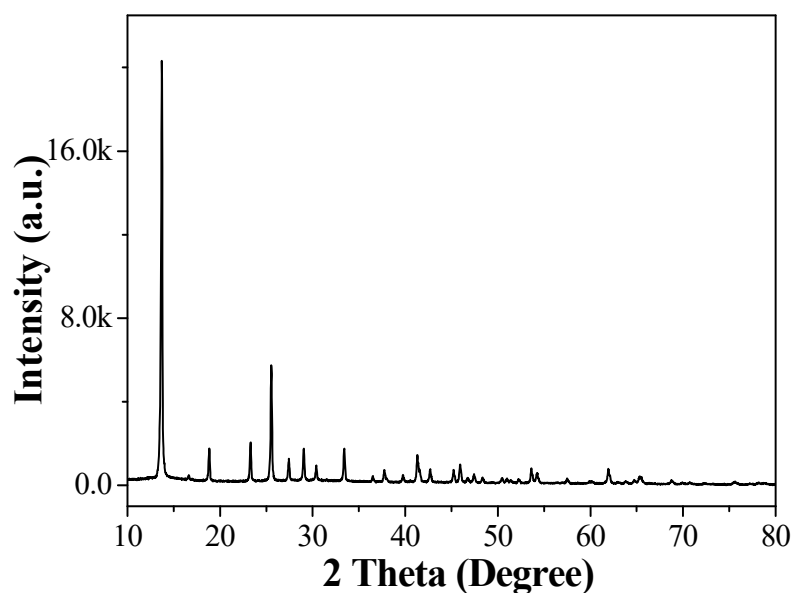


Fig. S2 XRD pattern of homogeneously precipitated zinc titanium glycolate acetate hydrate ($\text{Zn}_2\text{Ti}_3\text{-GAH}$).

Powder X-ray diffraction (XRD) pattern: monoclinic system, 2θ degree (int-f, hkl) = 13.715 (100, -101), 16.631 (1, -110), 18.838 (8, 020), 23.304(9, -120), 25.548(28, 111), 27.436 (5,-202), 29.037 (8, -212), 30.397 (4, 121), 33.419 (8, -222), 36.503 (1, -103), 37.755 (2, 112), 39.755(1, -232), 41.312 (7, 122), 41.551 (2, -303), 42.694 (3, -313), 45.227 (3, 141), 45.936 (4, -323), 46.762 (5, 132), 47.456 (1, -242), 48.327 (4, -204), 50.429 (3, 103), 50.976 (2, 033), 51.393 (<1, -314), 52.250 (1, -224), 53.621 (3, -243), 54.224 (1, -324), 57.488 (<1, 043), 59.952 (<1, 024), 61.951 (3, -305), 63.812 (<1, -162), 64.731 (<1, -344), 65.361 (1, -105), 68.745 (<1, -425), 69.945 (<1, 044), 70.768 (<1, -163), 75.633 (<1, -525).

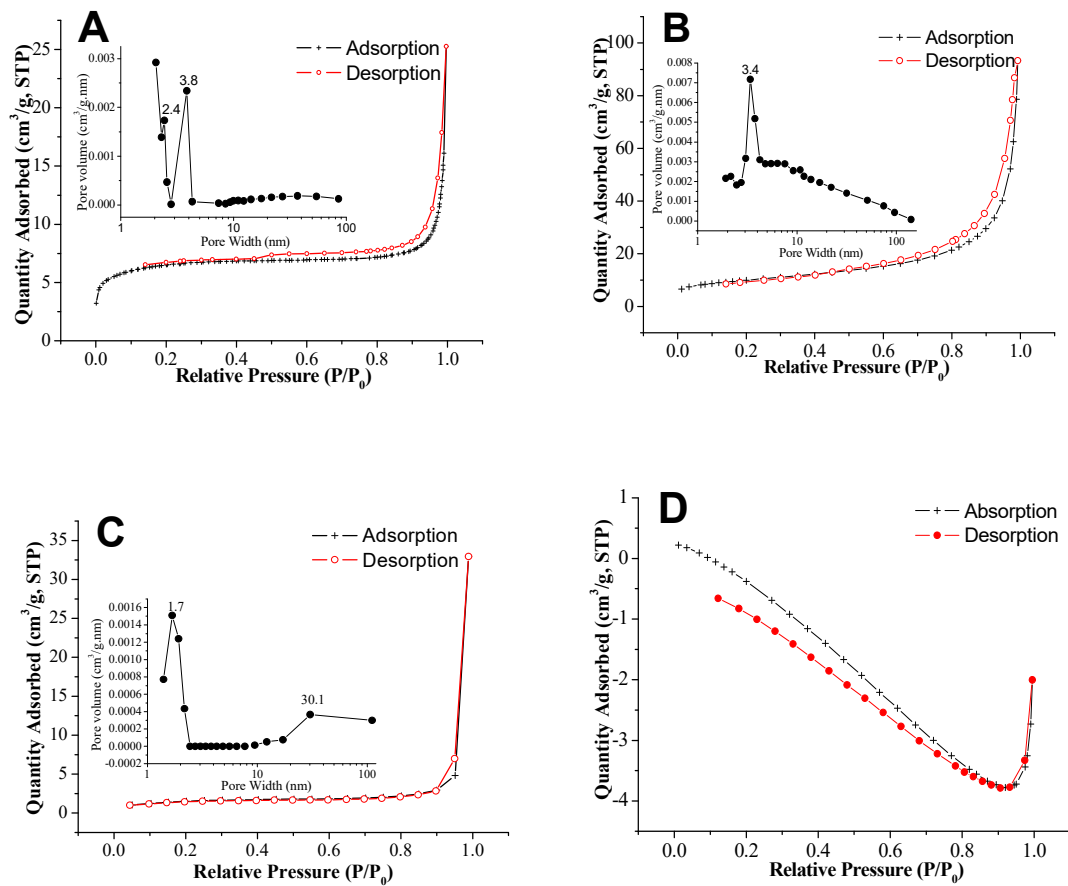
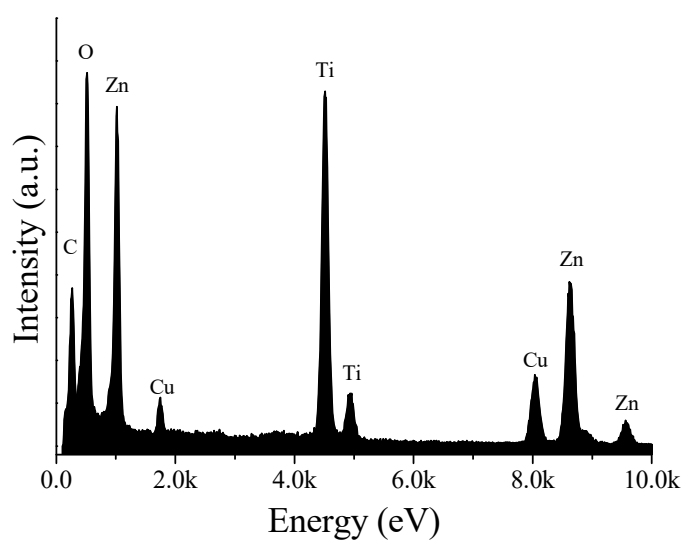


Fig. S3 N₂ adsorption–desorption isotherm at 77 K of Zn₂Ti₃-GAH (A) and zinc titanate via thermal treatment at 500 °C for 3 h (B, Zn₂Ti₃O₈), 700 °C for 2 h (C, r-TiO₂ supported h-ZnTiO₃) and 950 for 3 h (D, r-TiO₂ supported Zn₂TiO₄); Inset shows the corresponding pore size distribution by BJH method.



Elemental Analysis

Element	Weight %	Atomic %
Ti	53.00	23.95
Zn	47.00	15.57
Total	100	

The Ti : Zn Atomic ratio is $23.95 : 15.57 = 1.54$

Fig. S4 TEM-EDS spectra of $\text{Zn}_2\text{Ti}_3\text{-GAH}$ and the derived elemental analysis. Cu and partial C signals derived from the supported carbon coated copper grid for TEM analysis.

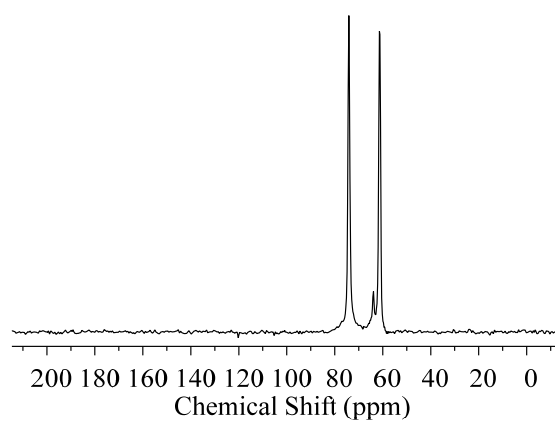


Fig. S5 CPMAS ^{13}C NMR spectrum of $\text{Zn}_2\text{Ti}_3\text{-GAH}$ showing resonances associated with the $[-\text{OCH}_2-]$ groups.

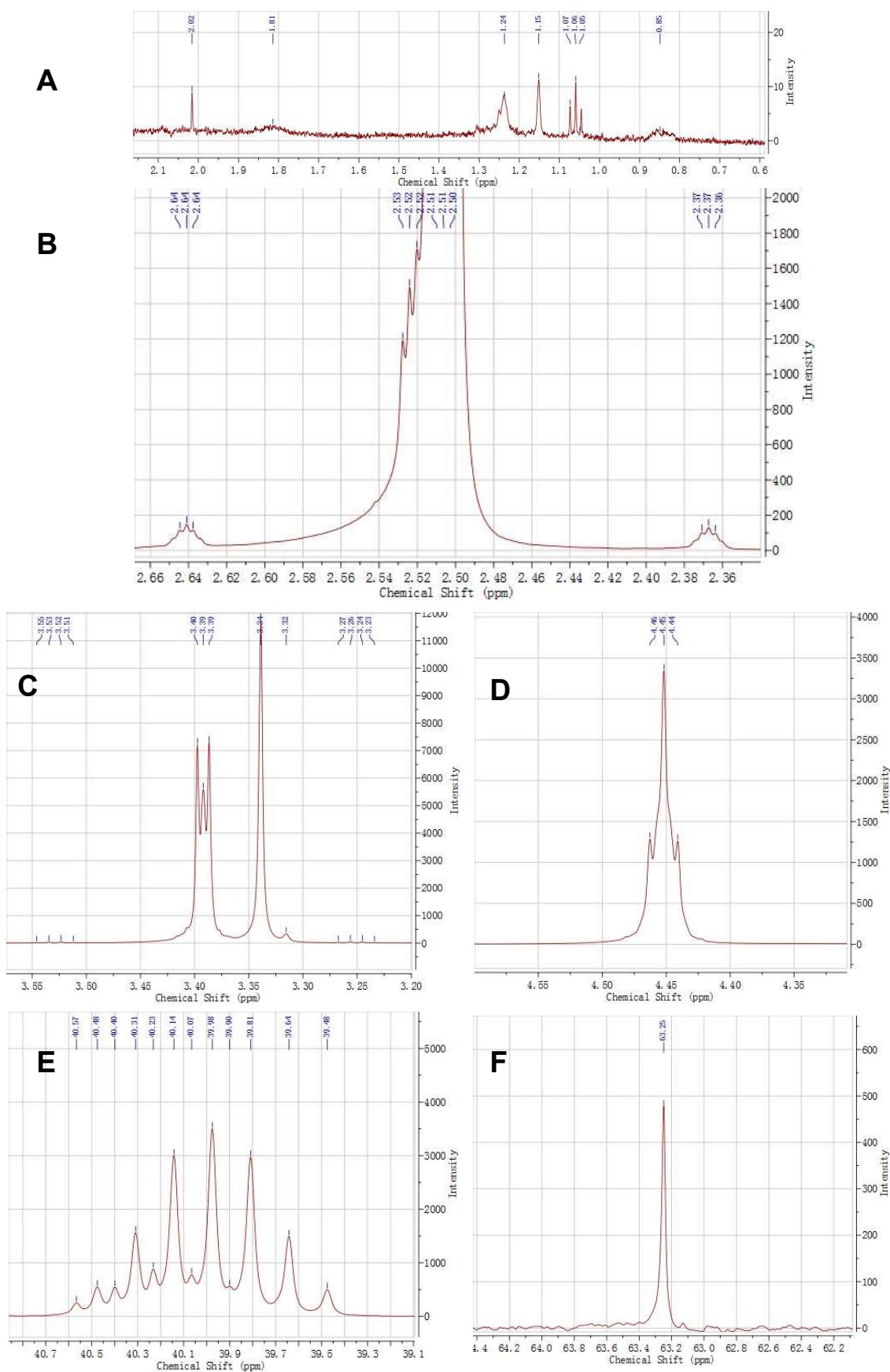


Fig. S6 solution ^1H (A-D) and ^{13}C (E-F) NMR spectra of $\text{Zn}_2\text{Ti}_3\text{-GAH}$ in deuterated DMSO ($(\text{CD}_3)_2\text{SO}$). The ^1H NMR: $\delta = 2.51$ (q, $J = 5$ Hz, CH_3), 3.34 (s, H_2O); ^{13}C NMR: $\delta = 39.98$ (sept, CH_3) come from the DMSO solvent.

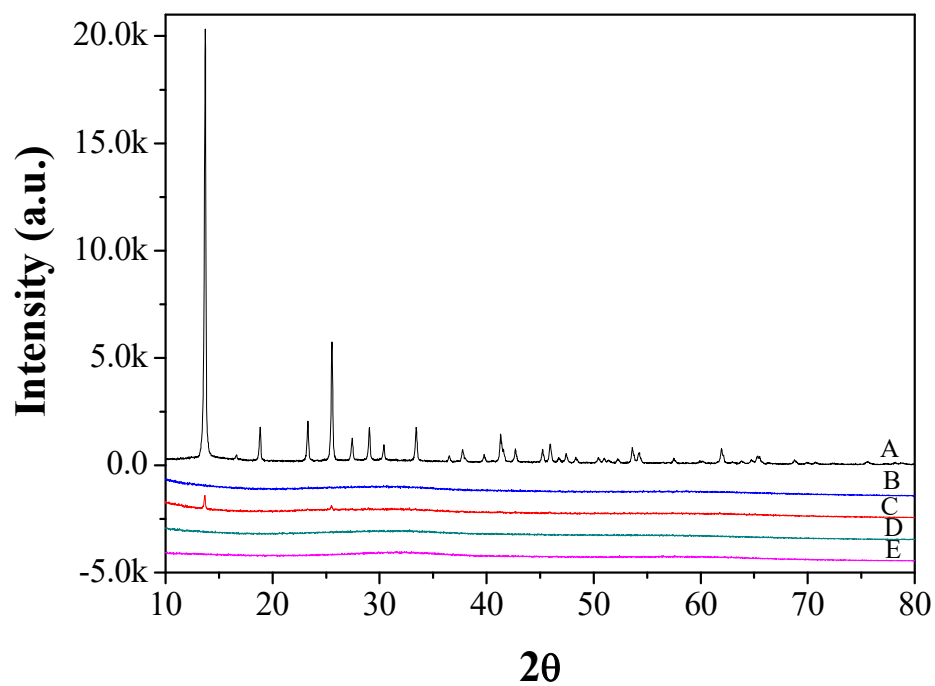


Fig. S7 XRD patterns of $\text{Zn}_2\text{Ti}_3\text{-GAH}$ before (A) and after immersing in DMSO (B), DMF (C, after one time soaking; D, after two times soaking) and H_2O (E) overnight.

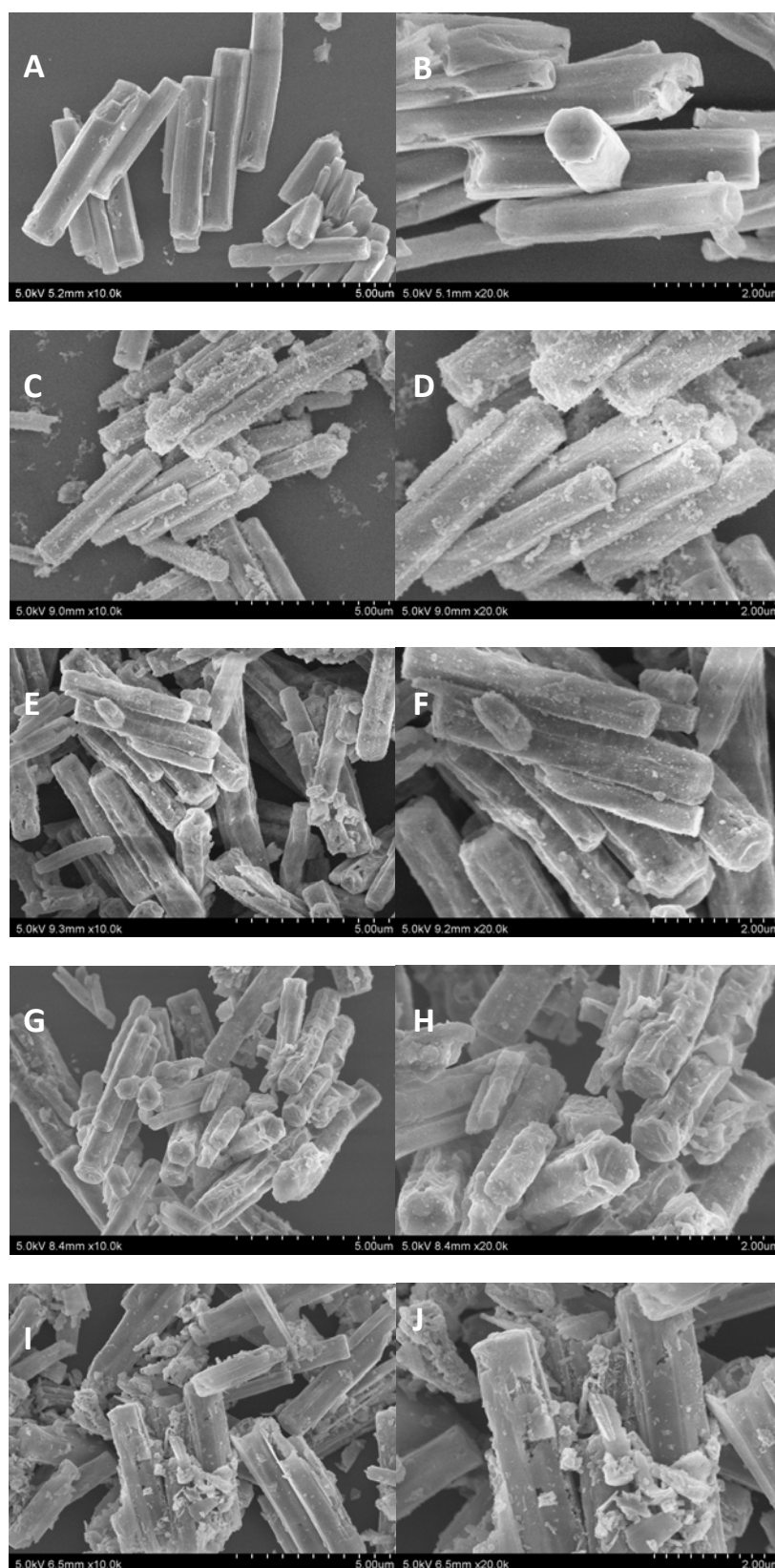


Fig. S8 SEM images of Zn₂Ti₃-GAH before (A, B) and after immersing in DMSO (C, D), DMF (E-H; E, F for one time soaking; G, H for two times soaking) and H₂O (I, J) overnight.

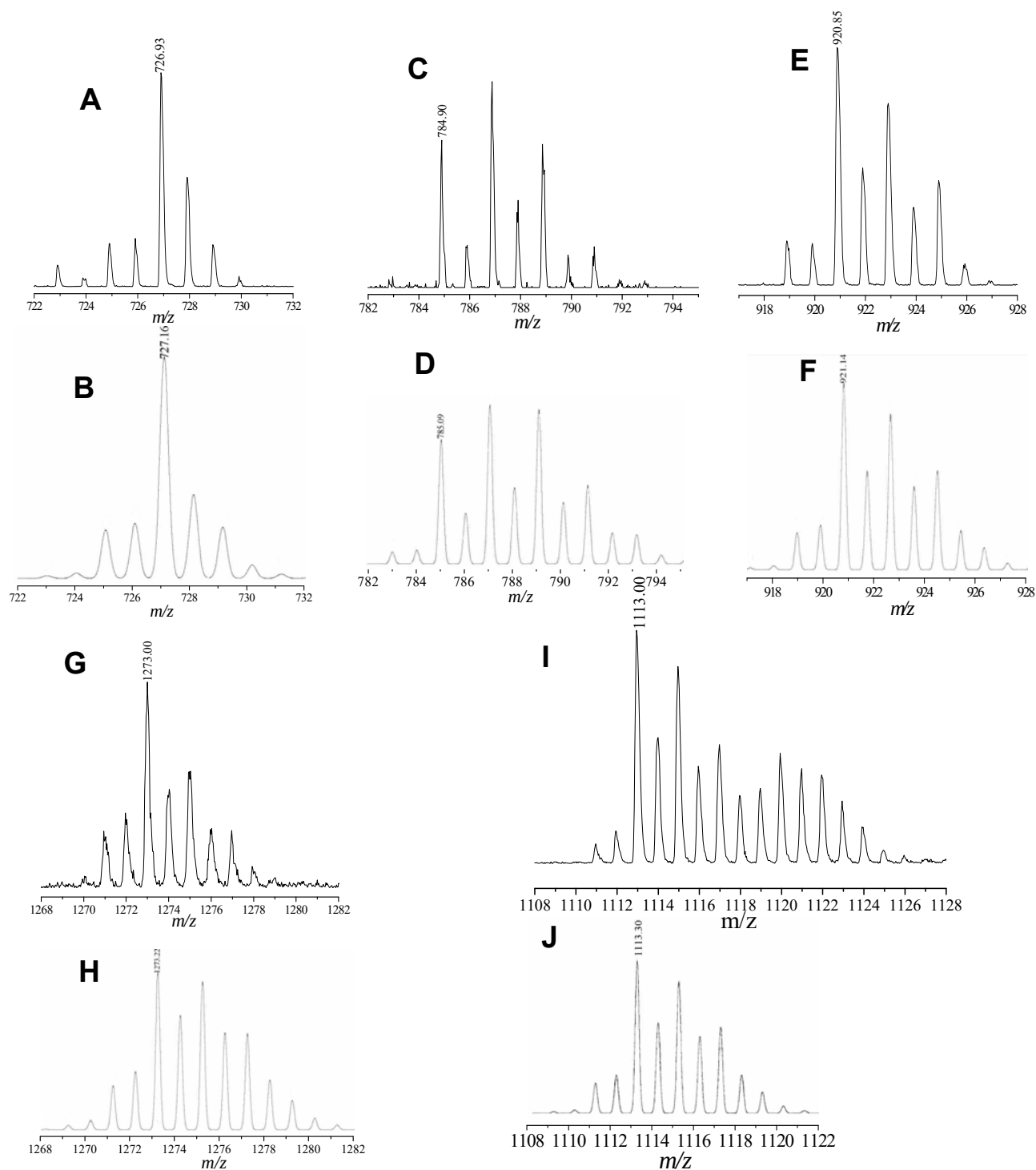
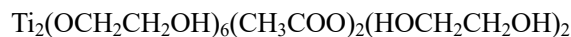
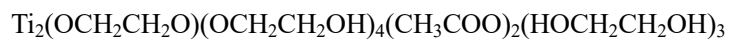
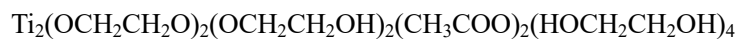


Fig. S9 (A-J) MS comparisons of the experimentally obtained isotopic distribution patterns with the calculated patterns of molecule ion peaks of other species detected after treating $\text{Zn}_2\text{Ti}_3\text{-GAH}$ with DMF, including (A,B) $\text{C}_{20}\text{H}_{48}\text{O}_{20}\text{Ti}_2$, (C,D) $\text{C}_{20}\text{H}_{48}\text{O}_{20}\text{TiZn}_2$, (E,F) $\text{C}_{24}\text{H}_{56}\text{O}_{26}\text{Ti}_2\text{Zn}$, (G,H) $\text{C}_{34}\text{H}_{80}\text{O}_{36}\text{Ti}_3\text{Zn}$, (I, J) $\text{C}_{30}\text{H}_{80}\text{O}_{32}\text{Ti}_2\text{Zn}$. Except for the last complex, all of the experimentally obtained isotopic distribution patterns matched well with the corresponding calculated pattern, while the calculated isotopic distribution pattern of the last complex (I, J) only matches the downfield shift of the experimental pattern due to spectral overlapping with another complex in the upfield shift. The possible molecular formulas were listed on the basis of the analysis of MS, starting materials and solvent used, molecular ligands determined by FTIR as well as charge balance held in the molecular formula.

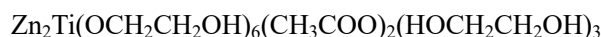
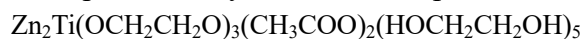
(A, B): $C_{20}H_{48}O_{20}Ti_2Na$, $[M+Na]^+$;

A: experimentally obtained isotopic distribution pattern; **B:** the calculated pattern;



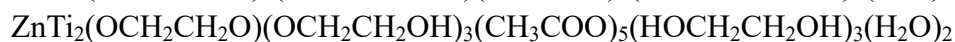
(C, D): $C_{20}H_{49}O_{20}TiZn_2$, $[M+H]^+$;

C: experimentally obtained isotopic distribution pattern; **D:** the calculated pattern;



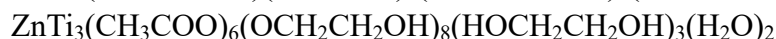
(E, F): $C_{24}H_{57}O_{26}Ti_2Zn$, $[M+H]^+$;

E: experimentally obtained isotopic distribution pattern; **F:** the calculated pattern;



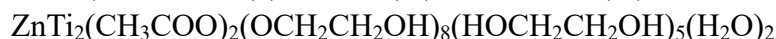
(G, H): $C_{34}H_{81}O_{36}Ti_3Zn$, $[M+H]^+$;

G: experimentally obtained isotopic distribution pattern; **H:** the calculated pattern;



(I, J): $C_{30}H_{81}O_{32}Ti_2Zn$, $[M+H]^+$;

I: experimentally obtained isotopic distribution pattern; **J:** the calculated pattern;



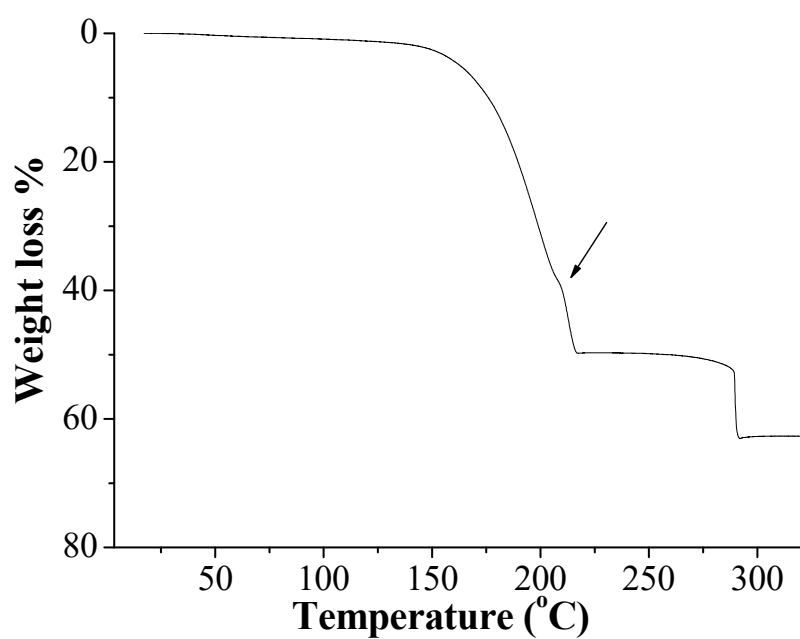


Fig. S10 The TG curve of Zn₂Ti₃-GAH in temperature range of 25-300 °C for showing the point of inflection between step 1 and 2 during thermal evolution, as indicated by the arrow.

Fig. S11 Thermal behaviors and analytical results from the TG-DTA curves of zinc titanium glycolate acetate hydrate ($\text{Zn}_2\text{Ti}_3\text{-GAH}$).

Thermal behavior	Temperature (°C) and Profile	Weight loss (%)	
		Obsd.	Calc. ^a
Endotherm (water and EG)	148-196, peak at 180 (weak)	39.0	39.3
Exothermal Combustion 1 (glycolate)	214 (strong and sharp)	10.6	9.9
Exothermal Combustion 2 (acetate)	291 (very strong and sharp)	13.1	15.5
Exotherm (Burning off the residual organic species and the crystallization of materials)	293-750, a long tail extending to higher temperature region, (weak and broad)	3.9	

^aCalculated weight loss was determined on the basis of the tentatively derived formula of $\text{Zn}_2\text{Ti}_3(\text{OCH}_2\text{CH}_2\text{O})_4(\text{OCH}_2\text{CH}_2\text{OH})_5(\text{CH}_3\text{COO})_3 \cdot 2\text{HOCH}_2\text{CH}_2\text{OH} \cdot \text{H}_2\text{O}$ where mass loss during the endothermic step was calculated by departure of $(\text{OCH}_2\text{CH}_2\text{OH})_5(\text{HOCH}_2\text{CH}_2\text{OH})_2(\text{H}_2\text{O})$ fragments; the mass loss of the combustion 1 was evaluated by only removing the carbon and hydrogen species in the glycolate ligands $[(\text{OCH}_2\text{CH}_2\text{O})_4]$; the mass loss of the combustion 2 was calculated by the removal of the whole acetate groups $[(\text{CH}_3\text{COO})_3]$.

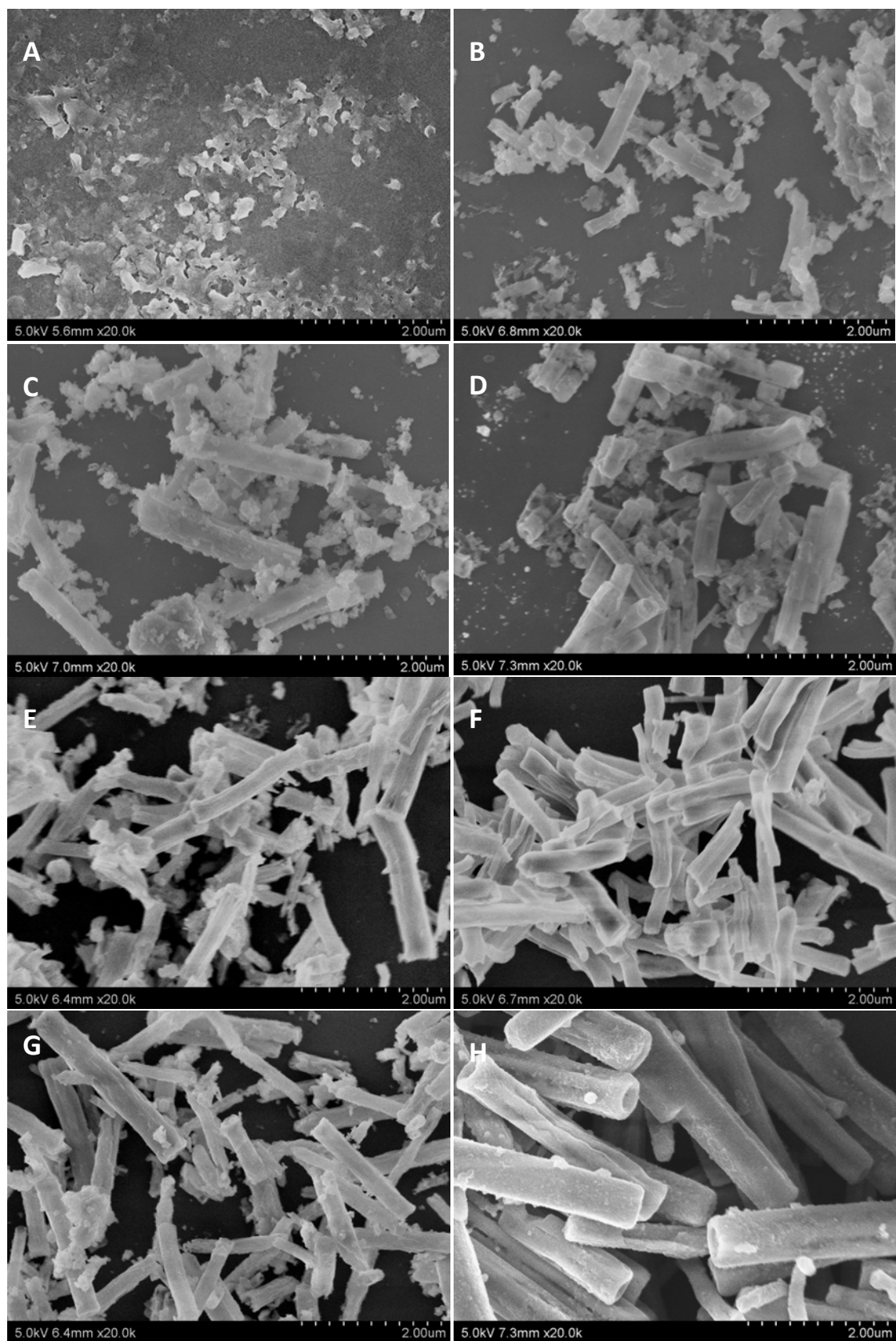


Fig. S12 SEM images of products by sampling at different periods of reaction time when synthesizing $\text{Zn}_2\text{Ti}_3\text{-GAH}$. (A) 1 h; (B) 1 h 30 min; (C) 1 h 50 min; (D) 2 h 10 min; (E) 2 h 40 min; (F) 3 h 10 min; (G) 4 h 10 min; (H) after further aging for 12 h.

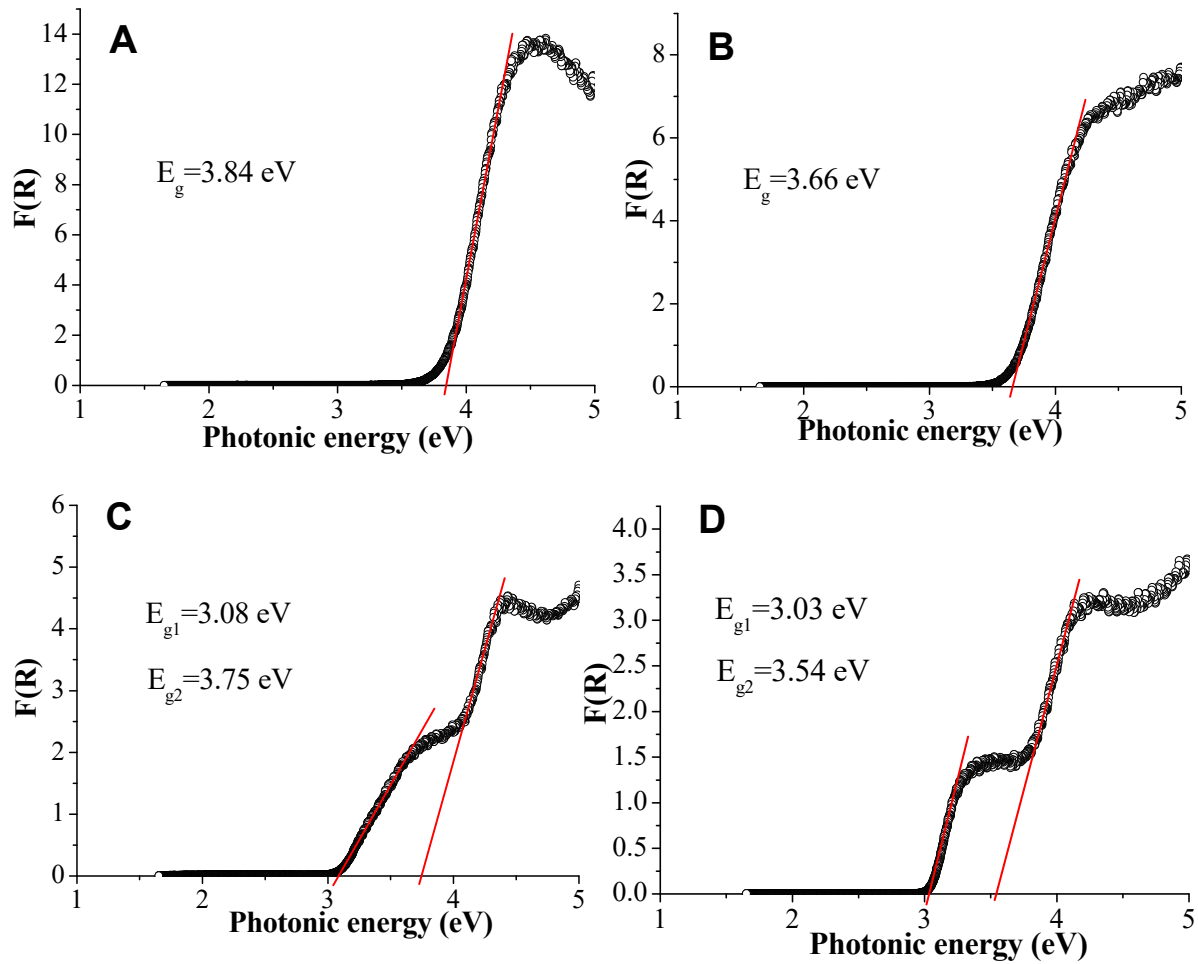


Fig. S13 Determination of the band gaps of $\text{Zn}_2\text{Ti}_3\text{-GAH}$ (A), $\text{Zn}_2\text{Ti}_3\text{O}_8$ (B, via thermal treatment of $\text{Zn}_2\text{Ti}_3\text{-GAH}$ at 500 °C for 3 h), r-TiO_2 supported h-ZnTiO_3 (C, via thermal treatment of $\text{Zn}_2\text{Ti}_3\text{-GAH}$ at 700 °C for 2 h) and r-TiO_2 supported Zn_2TiO_4 (D, via thermal treatment of $\text{Zn}_2\text{Ti}_3\text{-GAH}$ at 950 °C for 3 h) using direct analysis of the absorption edges, by extrapolation to the energy axis.