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 acetatehydrate (Zn$_2$Ti$_3$-GAH).
Fig. S2 XRD pattern of homogeneously precipitated zinc titanium glycolate acetate hydrate (Zn$_2$Ti$_3$-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 N$_2$ adsorption–desorption isotherm at 77 K of Zn$_2$Ti$_3$-GAH (A) and zinc titanate via thermal treatment at 500 °C for 3 h (B, Zn$_2$Ti$_3$O$_8$), 700 °C for 2 h (C, r-TiO$_2$ supported h-ZnTiO$_3$) and 950 for 3 h (D, r-TiO$_2$ supported Zn$_2$TiO$_4$); Inset shows the corresponding pore size distribution by BJH method.
<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>53.00</td>
<td>23.95</td>
</tr>
<tr>
<td>Zn</td>
<td>47.00</td>
<td>15.57</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

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

**Fig. S4** TEM-EDS spectra of Zn$_2$Ti$_3$-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 Zn$_2$Ti$_3$-GAH showing resonances associated with the [-OCH$_2$-] groups.
Fig. S6 solution $^1$H (A-D) and $^{13}$C (E-F) NMR spectra of Zn$_2$Ti$_3$-GAH in deuterated DMSO ((CD$_3$)$_2$SO). The $^1$H NMR: δ= 2.51 (q, $J$ = 5 Hz, CH$_3$), 3.34 (s, H$_2$O); $^{13}$C NMR: δ= 39.98 (sept, CH$_3$) come from the DMSO solvent.
Fig. S7 XRD patterns of Zn$_2$Ti$_3$-GAH before (A) and after immersing in DMSO (B), DMF (C, after one time soaking; D, after two times soaking) and H$_2$O (E) overnight.
Fig. S8 SEM images of Zn$_2$Ti$_3$-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 H$_2$O (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 Zn$_2$Ti$_3$-GAH with DMF, including (A,B) C$_{20}$H$_{48}$O$_{20}$Ti$_2$, (C,D) C$_{20}$H$_{48}$O$_{20}$TiZn$_2$, (E,F) C$_{24}$H$_{56}$O$_{26}$Ti$_2$Zn, (G,H) C$_{34}$H$_{80}$O$_{36}$Ti$_3$Zn, (I, J) C$_{30}$H$_{80}$O$_{32}$Ti$_2$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_{2}Na, [M+Na]^+;
A: experimentally obtained isotopic distribution pattern; B: the calculated pattern;
Ti_{2}(OCH_{2}CH_{2}O)_{3}(CH_{3}COO)_{2}(HOCH_{2}CH_{2}OH)_{5}
Ti_{2}(OCH_{2}CH_{2}O)_{2}(OCH_{2}CH_{2}OH)_{2}(CH_{3}COO)_{2}(HOCH_{2}CH_{2}OH)_{4}
Ti_{2}(OCH_{2}CH_{2}O)(OCH_{2}CH_{2}OH)_{3}(CH_{3}COO)_{2}(HOCH_{2}CH_{2}OH)_{3}
Ti_{2}(OCH_{2}CH_{2}OH)_{6}(CH_{3}COO)_{2}(HOCH_{2}CH_{2}OH)_{2}

(C, D): C_{20}H_{49}O_{20}TiZn_{2}, [M+Na]^+;
C: experimentally obtained isotopic distribution pattern; D: the calculated pattern;
Zn_{2}Ti_{2}(OCH_{2}CH_{2}O)_{3}(CH_{3}COO)_{2}(HOCH_{2}CH_{2}OH)_{5}
Zn_{2}Ti_{2}(OCH_{2}CH_{2}O)_{2}(OCH_{2}CH_{2}OH)_{2}(CH_{3}COO)_{2}(HOCH_{2}CH_{2}OH)_{4}
Zn_{2}Ti_{2}(OCH_{2}CH_{2}O)(OCH_{2}CH_{2}OH)_{3}(CH_{3}COO)_{2}(HOCH_{2}CH_{2}OH)_{4}
Zn_{2}Ti_{2}(OCH_{2}CH_{2}OH)_{6}(CH_{3}COO)_{2}(HOCH_{2}CH_{2}OH)_{3}

(E, F): C_{24}H_{57}O_{26}TiZn, [M+H]^+;
E: experimentally obtained isotopic distribution pattern; F: the calculated pattern;
Zn_{2}Ti_{2}(OCH_{2}CH_{2}O)_{3}(OCH_{2}CH_{2}OH)(CH_{3}COO)_{2}(HOCH_{2}CH_{2}OH)_{5}(H_{2}O)_{2}
Zn_{2}Ti_{2}(OCH_{2}CH_{2}O)(OCH_{2}CH_{2}OH)_{3}(CH_{3}COO)_{2}(HOCH_{2}CH_{2}OH)_{5}(H_{2}O)_{2}
Zn_{2}Ti_{2}(OCH_{2}CH_{2}O)(CH_{3}COO)_{5}(HOCH_{2}CH_{2}OH)_{2}(H_{2}O)_{2}

(G, H): C_{34}H_{81}O_{36}Ti_{3}Zn, [M+H]^+;
G: experimentally obtained isotopic distribution pattern; H: the calculated pattern;
Zn_{3}Ti_{3}(OCH_{2}CH_{2}O)_{4}(CH_{3}COO)_{6}(HOCH_{2}CH_{2}OH)_{7}(H_{2}O)_{2}
Zn_{3}Ti_{3}(OCH_{2}CH_{2}O)_{3}(OCH_{2}CH_{2}OH)_{6}(OCH_{2}CH_{2}OH)_{5}(HOCH_{2}CH_{2}OH)_{5}(H_{2}O)_{2}
Zn_{3}Ti_{3}(OCH_{2}CH_{2}O)_{2}(CH_{3}COO)_{6}(OCH_{2}CH_{2}OH)_{4}(HOCH_{2}CH_{2}OH)_{6}(H_{2}O)_{2}
Zn_{3}Ti_{3}(OCH_{2}CH_{2}O)(CH_{3}COO)_{6}(CH_{3}COO)_{5}(HOCH_{2}CH_{2}OH)_{6}(H_{2}O)_{2}

(I, J): C_{30}H_{81}O_{32}Ti_{2}Zn, [M+H]^+;
I: experimentally obtained isotopic distribution pattern; J: the calculated pattern;
Zn_{2}Ti_{2}(OCH_{2}CH_{2}O)_{4}(CH_{3}COO)_{2}(HOCH_{2}CH_{2}OH)_{6}(H_{2}O)_{2}
Zn_{2}Ti_{2}(OCH_{2}CH_{2}O)_{3}(CH_{3}COO)_{2}(OCH_{2}CH_{2}OH)_{2}(HOCH_{2}CH_{2}OH)_{5}(H_{2}O)_{2}
Zn_{2}Ti_{2}(OCH_{2}CH_{2}O)_{2}(CH_{3}COO)_{2}(OCH_{2}CH_{2}OH)_{4}(HOCH_{2}CH_{2}OH)_{6}(H_{2}O)_{2}
Zn_{2}Ti_{2}(OCH_{2}CH_{2}O)(CH_{3}COO)_{2}(OCH_{2}CH_{2}OH)_{6}(HOCH_{2}CH_{2}OH)_{6}(H_{2}O)_{2}
Zn_{2}Ti_{2}(CH_{3}COO)_{2}(OCH_{2}CH_{2}OH)_{6}(HOCH_{2}CH_{2}OH)_{5}(H_{2}O)_{2}
**Fig. S10** The TG curve of Zn$_2$Ti$_3$-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 (Zn$_2$Ti$_3$-GAH).

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

$^a$Calculated weight loss was determined on the basis of the tentatively derived formula of Zn$_2$Ti$_3$(OCH$_2$CH$_2$O)$_4$(OCH$_2$CH$_2$OH)$_5$(CH$_3$COO)$_3$$^2$HOCH$_2$CH$_2$OH•H$_2$O where mass loss during the endothermic step was calculated by departure of (OCH$_2$CH$_2$OH)$_5$(HOCH$_2$CH$_2$OH)$_2$(H$_2$O) fragments; the mass loss of the combustion 1 was evaluated by only removing the carbon and hydrogen species in the glycolate ligands [(OCH$_2$CH$_2$O)$_4$]; the mass loss of the combustion 2 was calculated by the removal of the whole acetate groups [(CH$_3$COO)$_3$].
Fig. S12 SEM images of products by sampling at different periods of reaction time when synthesizing Zn$_2$Ti$_3$-GAH. (A) 1 h; (B) 1 h 30 min; (C) 1 h 50 min; (D) 2 h 10 min; (E) 2 h 40 min; (F) 3 h 10 min; (G) 4 h 10 min; (H) after further aging for 12 h.
Fig. S13 Determination of the band gaps of Zn$_2$Ti$_3$-GAH (A), Zn$_2$Ti$_3$O$_8$ (B, via thermal treatment of Zn$_2$Ti$_3$-GAH at 500 °C for 3 h), r-TiO$_2$ supported h-ZnTiO$_3$ (C, via thermal treatment of Zn$_2$Ti$_3$-GAH at 700 °C for 2 h) and r-TiO$_2$ supported Zn$_2$TiO$_4$ (D, via thermal treatment of Zn$_2$Ti$_3$-GAH at 950 °C for 3 h) using direct analysis of the absorption edges, by extrapolation to the energy axis.