

Electronic Supplementary Information for

Synergetic photocatalyst derived from porous organo Ti-O clusters pillared graphene oxide frameworks (GOFs)

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1. Experimental Details

Materials. Chemicals: Graphite powder (Aldrich, 1-2 μm), NaNO_3 (Wako special grade), H_2SO_4 (min. 95%, Wako special grade), HCl (36%, Wako analytical grade), HF (50%, Wako special grade), KMnO_4 (Kanto Kagaku special grade), anhydrous ethanol (>95.5%, Wako Pharmacopoeia grade), H_2O_2 (50%, Wako special grade), $\text{Ti}(\text{O}i\text{Bu})_4$ (Wako first grade), methyl orange (Wako special grade). All these chemicals are used as received without further purification. Deionized water was used throughout the experiment procedure.

Synthesis.

1) Synthesis of GO sample

The GO sample was synthesized by a modified Hummer's method. Typically, 0.75 g of graphite powder, 4.5 g of NaNO_3 and 30 mL of concentrated H_2SO_4 were added to a beaker in an ice bath. The mixture was magnetically stirred, and 4.5g of KMnO_4 was slowly added. The beaker was transferred into a water bath and heated at controlled temperature (35 ± 5 °C). After five-hour aging, 60 mL of deionized water was added, and the mixture was moved to an oil bath and further aged at 80 °C for one hour. Subsequently, 3.0 mL of H_2O_2 was dropped in, following which another portion of 100 mL of H_2O was added. The warm mixture was filtered, washed with 100 mL of HCl

solution (10%) and deionized water until the pH of the filtrate reached to 6. The product was dried at room temperature, collected and stored in a sample vial for further use.

2) Synthesis of the organo Ti-O cluster pillared graphene oxide framework (GOF)

0.2 g of GO powder was added to 50 mL of absolute ethanol. The mixture was subjected to ultrasonical treatment for 20 minutes to prompt the dispersion of GO sheets. The organo-titanium solution was prepared by dissolving 2.46 g of $\text{Ti}(\text{O}i\text{Bu})_4$ in 100 mL of absolute ethanol. After stirring for 10 minutes to form a transparent solution, the GO dispersion was added dropwise into the $\text{Ti}(\text{O}i\text{Bu})_4$ solution under stirring. The obtained mixture was then transferred to an oil bath and refluxed at 60 °C for five hours. The product was recovered by centrifugation, re-dispersed and washed by ethanol for three times to remove the excessive $\text{Ti}(\text{O}i\text{Bu})_4$ reagent, and finally dried in an oven at 60 °C. The product was stored in a tightly capped glass vial to avoid contacting with moisture.

3) Synthesis of TiO_2 nanoplates/lamellar carbon composite

In a typical synthesis, 0.1 g of pillared GO framework was dispersed to 20 mL of ethanol. The mixture was subjected to ultrasonic treatment for 20 minutes, after which 200 μL of deionized water was added. The mixture was transferred to a Teflon-lined autoclave (25 mL in volume), sealed and heat-treated at 180 °C for 24 hours. The product was recovered by centrifugation, washed by diluted water, and finally dried at 60 °C.

In another modified synthesis, HF solution (50%) was employed to control the size of TiO_2 nanoplates, A mixture of HF (75 μL) and H_2O (125 μL) was applied instead of pure deionized water. The other steps were identical to the typical procedure described above.

Characterizations.

X-ray diffraction (XRD) data were recorded on a Rigaku Smartlab diffractometer equipped with a $\text{Cu K}\alpha$ source operating at 30 mA and 40 KV.

The microstructures of the samples were investigated by an analytical Topcon EM-002B-type transmission electron microscope (TEM) operated at 120kV, equipped

with energy dispersive X-ray spectroscopy (EDS). The EDS analyses were carried out by using Thermo Fisher Scientific NORAN System 7 EDS analysis system. The high-resolution TEM (HRTEM) images were observed by the FEI Tecnai Osiris-type transmission electron microscope, operated at 200kV. The specimen was prepared by ultrasonically dispersing the samples in ethanol followed by dropping the sample-contained suspension on carbon-coated Cu grids.

Thermogravimetric analyses (TG) were carried out in air at a heating rate of 5 K/minute using a Rigaku TG8120 apparatus with a reference of commercial α -Al₂O₃.

N₂ adsorption isotherms were measured at 77K on a commercial Belsorp Max-type volumetric apparatus (Japan Bell Co.). Samples were preevacuated at 353 K for 24 hours for the pillared sample and at 393 K for 2 hours for the solvothermal derivatives before adsorption.

For the solid state ¹³C-NMR experiment, the samples were packed in a ceramic rotor, and the NMR spectra were measured by the CP/MAS method (Chemagnetics CMX-300 solid-state NMR spectrometer). The 90° ¹H pulse width was 3.7 us, the ¹³C frequency was 75.58 MHz, the MAS rate was 10 kHz, the number of scans was 2500-80000, the contact time was 1 ms, and the pulse delay was 4 s. Chemical shifts were calibrated, with respect to tetramethylsilane, using the hexamethylbenzene methyl group peak at 17.4 ppm as an external standard.

Photocatalytic experiments.

The photodecomposition behaviour of methyl orange (MO) from aqueous solution by the TiO₂/layered carbon composite was evaluated in the following procedure: 5 mg of powdered sample was dispersed to 9 mL of methyl orange solution (concentration: 20 mg/mL). The mixture was tightly capped in a quartz tube (volume of 10mL), shaken in a dark box under a constant temperature of 30 °C. After 24-hour storing, the sample was subjected to UV-irradiation (UV-C, 254 nm, 30W) for a counted time. The catalyst was separated from the aqueous solution by centrifugation, and the concentration of the residue MO in supernatant liquid was determined from the

absorbance at 448 nm. The apparent rate constants were calculated from the time course of concentration based on the 1st order kinetics.

2. Figures and Table

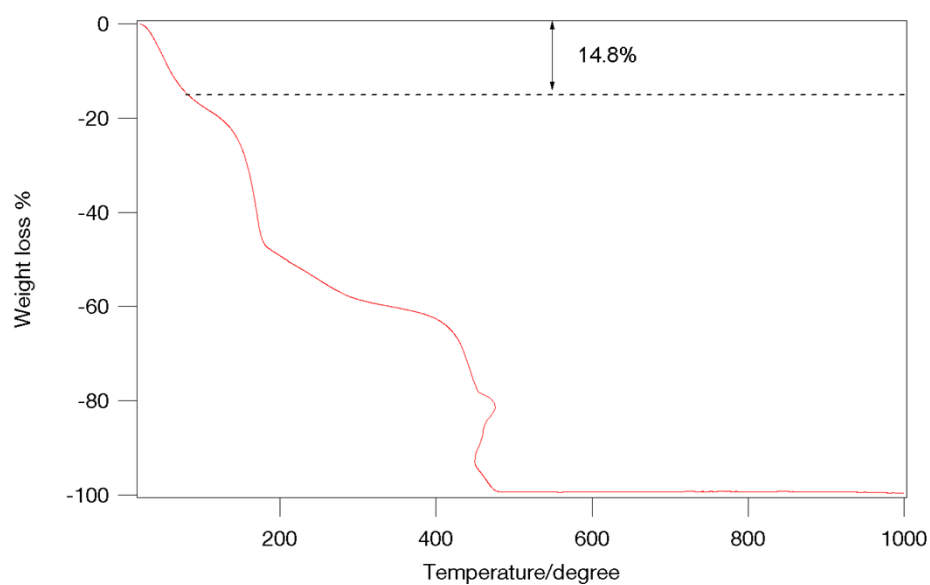


Figure S1. TG data of the GO sample. The water content was estimated as 14.8%.

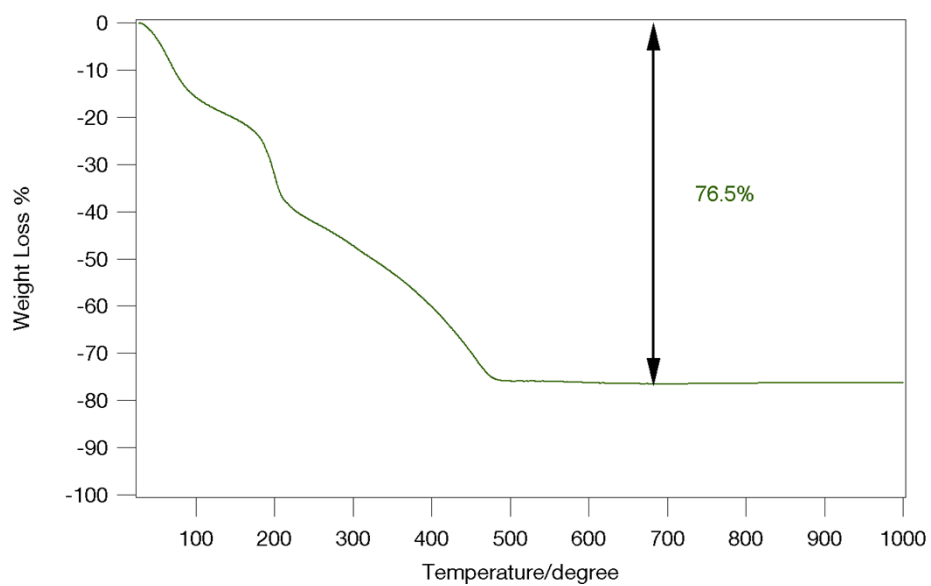


Figure S2. TG data of the organo Ti-O cluster pillared GOF sample. Weight loss of 76.5% after the sample is heated to 1000 degree supports the intercalation.

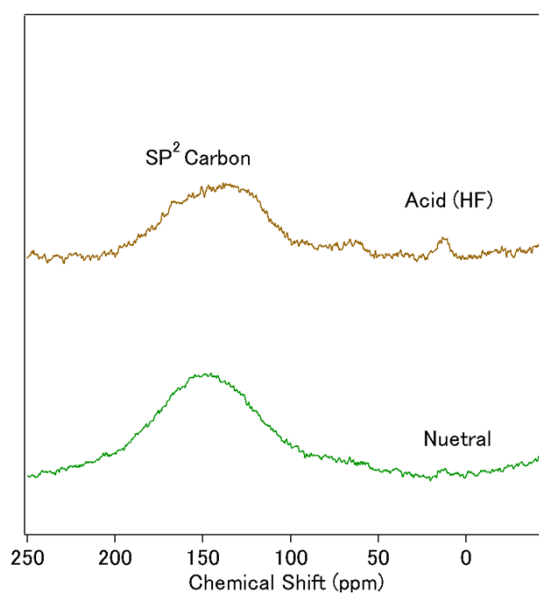


Figure S3. ¹³C-NMR spectra of the TiO₂/layered carbon composites prepared at neutral and acidic condition in the presence of HF.

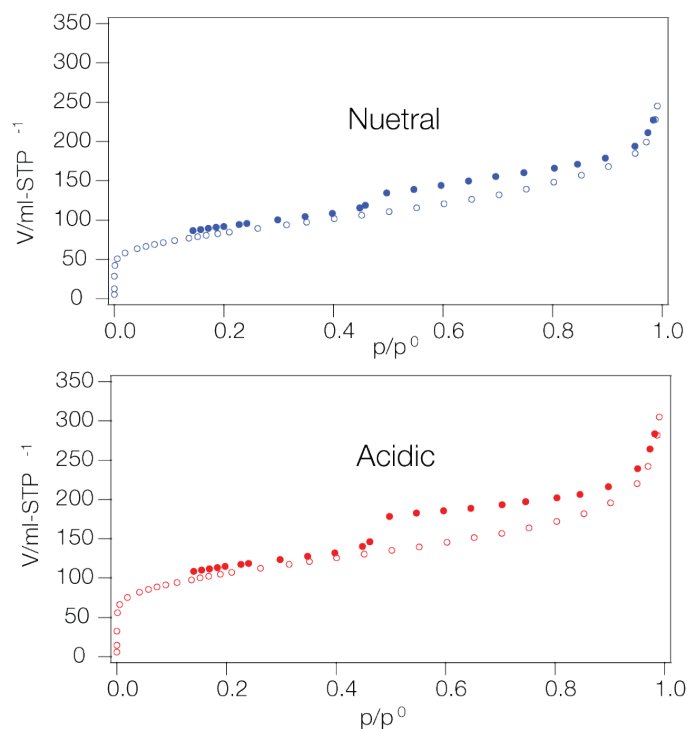


Figure S4. N₂ adsorption-desorption isotherm at 77 K on the TiO₂/layered carbon composite prepared at neutral and acidic conditions. The values of specific surface area calculated are 294 and 375 m²·g⁻¹ for the samples prepared at neutral and acidic conditions, respectively.

Table S1. TiO₂ content (W_{TiO_2}), MO adsorption (W_{MO}), and rate constant (r ,) for the photocatalytic reactions of MO.

	W_{TiO_2} (100%)	$W_{\text{MO}}/\text{mg} \cdot \text{g}^{-1}$	$r, / \text{min}^{-1}$
P-25	100	3.1	0.269
Neutral	45	14.2	0.142
HF	27	32.8	0.288