Supplementary Information

TiO$_2$-pillared Clays with Well-ordered Porous Structure and Excellent their Photocatalytic Activity

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Experimental

Materials

The synthetic Na-fluoromica (denoted as Na-mica) with a chemical formula of $Na_{0.7}Mg_{2.65}Si_4O_{10}F_2$ and the natural Na-montmorillonite (Kunipia-G) with a chemical formula of $Na_{0.35}K_{0.01}Ca_{0.02}(Si_{3.89}Al_{0.11})(Al_{1.60}Mg_{0.32}Fe_{0.08})O_{10}(OH)_2$ were purchased from CO-OP Chemical Co. Ltd. and Kunimine Industries Co. Ltd., respectively, and used as the host for pillaring TiO_2 nanoparticles without any purification. Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, 98%), iron(II) chloride ($FeCl_2$, 98%), and titanium tetraisopropoxide (97%, $Ti(OCH(CH_3)_2)_4$) were purchased from Sigma-Aldrich. Hydrochloric acid was purchased from Daejung Chemical and Metals. All the chemicals were used without any further purification.

Synthesis of Materials

Clays with different optical transparency.   Based on the Hoffman-Klemen effect, optical transparency and cation exchange capacity of the pristine clay were carefully controlled. Briefly, 5 g of Na-mica dispersed in 400 mL of deionized water was mixed with 0.5 mmol of $MgCl_2$ and $FeCl_2$, respectively, and each suspension was stirred at room temperature for 20 h. The partially exchanged Na-mica with Mg^{2+} or Fe^{2+} was separated by the centrifugation and thoroughly washed with deionized water until chloride ions in the supernatant were not be detected. Thus, the as-prepared samples were freeze-dried and finally calcined at 550 °C for 4 h in order to fix the Mg^{2+} or Fe^{2+} ions into the vacant octahedral sites in-plane of the clay lattice. The resulting samples with different transparency were denoted as MgM and FeM, respectively. The cationic exchange capacities of the as-prepared MgM and FeM and the pristine clays, Na-mica and Kunipia-G, were evaluated by the methylene blue method.[s1]

Clays with different porosity. TiO_2-pillared clays were synthesized via ion-exchange reaction and subsequent calcination (pillaring) as described previously by Yamanaka *et al*.[s2] At first, 2 g of each clay with different transparency (Na-mica, MgM, FeM and Kunipia-G) was dispersed in 200 mL deionized water and swelled for 12 h prior to ion-exchange reaction. We prepared TiO_2 oligomeric cations via the acid catalyzed hydrolysis based on Yamanaka's,[S2] where titanium isopropoxide was hydrolyzed and peptized with 1 N HCl (aq) to form the oligomeric cations (TiO_2 nanosol). The most important synthetic parameter for preparing TiO_2 nanosol with homogeneous size and charge was the ratio of HCl/Ti, which should be not less than 2. Under this condition, the hydrolyzed white slurry was transformed into a clear sol within 1 hour. In this study, titanium tetraisopropoxide was dropwisely added into 1 M HCl solution with HCl/Ti molar ratio of 2 and peptized at room temperature for 1 h and filtered with 0.2 μm PTEF membrane filter. The resulting TiO_2 nanosol was slowly added to 1 wt% aqueous suspension of clays with Ti/CEC ratio of 40, and ion-exchange reaction was carried out at 50 °C for 3 h. The resulting products were separated by centrifugation and washed with deionized water several times to remove the excess TiO_2 sol particles and chloride ions. The resulting TiO_2-pillared mica, TiO_2-pillared MgM, TiO_2-pillared FeM, and TiO_2-pillared Kunipia-G with different porosity were freeze-dried and calcined in the temperature range of 100–800 °C for 3 h (hereafter denoted as TM-X, TMgM-X, TFeM-X, and TK-X, where X is the calcination temperature).

Characterization

X-ray diffraction (XRD) patterns for all the samples were recorded using a Rigaku RINT-Ultima III diffractometer equipped with Ni-filtered Cu-Kα radiation (λ = 1.5405 Å) operated at 40 kV and 30 mA. The diffuse reflectance UV-vis spectra were measured using a Jasco V-550 spectrophotometer equipped with an integrating sphere by using $BaSO_4$ plate as the baseline. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100F HRTEM at an accelerating voltage of 200 kV. Cross-sectioned samples for the TEM analysis were prepared using a RMC Ultramicrotome (PowerTome PC), in which sectioning was conducted at RT with the thickness of 80 nm and speed of 0.5 mm/min. N_2 adsorption-desorption isotherms were volumetrically measured at liquid nitrogen temperature (77 K) using a Belsorp-Mini II (Bel Japan, Inc.). All the samples were degassed at 200 °C for 3 h under vacuum (< 10^{-2} torr) prior to the measurement. The chemical compositions were determined by measuring the X-ray fluorescence spectra for the pellet samples using a ZSX Primus II (wavelength dispersive type XRF instrument, Rigaku). The chemical analysis results were listed in Table S1 of the supporting information (ESI†). X-ray absorption spectroscopic (XAS) experiments at the Ti K-edge were performed using an X-ray absorption fine structure (XAFS) facility installed at beam line 10C in Pohang Accelerator Laboratory (PAL), Korea. XAS data were collected at room temperature in the transmission mode using gas-ionization detectors. All the spectra of Ti K-edge were calibrated by measuring the spectrum of Ti metal foil, simultaneously together with those of the samples. A Si(111) double crystal monochromator (DCM) was employed to monochromatize the X-ray photon energy. A step size of 0.2 eV in the X-ray absorption near edge structure (XANES) region was used to accurately collect XANES spectra. Data analyses for the experimental spectra were carried out by the standard procedure as reported previously.[s3] On the other hand, the extended X-ray absorption fine structure (EXAFS) analyses were also conducted by using the UWXAFS 2.0 code.[s4]

Photocatalytic activity test

Photocatalytic activity for all the samples was evaluated by the photodecomposition of methyl orange (MO) in a solution under UV light. Briefly, 30 mg of the samples were dispersed in 30 mL of an aqueous solution (5×10^{-5} M) of MO contained in a Pyrex glass vessel and the suspension was stirred for 30 min in the dark. 300 W Xe arc lamp was used and equipped with water filter to remove the infrared irradiation. The integrated light intensity between 290 nm and 800 nm was ~0.1 W/cm^2. The concentration of MO was determined by monitoring the absorbance at 464 nm (λ_{max} of MO) using a Perkin-Elmer Lamda 35 spectrophotometer.

References

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Table S1. Chemical composition of TiO$_2$-pillared clays and host clays obtained by XRF (x-ray fluorescence) analysis.

Samples	Chemical composition (wt%)					
	Na$_2$O	MgO	Al$_2$O$_3$	SiO$_2$	Fe$_2$O$_3$	TiO$_2$
Kunipia-G	2.67	2.53	24.96	67.00	2.85	-
Na-Mica	4.36	23.40	-	70.62	-	-
MgM	3.30	24.84	-	71.12	-	-
FeM	3.67	24.30	-	70.64	1.28	-
TM-500	1.32	16.22	-	46.73	-	34.96
TMgM-500	1.12	17.76	-	48.99	-	31.93
TFeM-500	1.46	16.72	-	48.30	0.63	32.28
TK-500	-	1.24	11.18	29.26	1.16	56.90

Table S2. Porous texture of TiO_2 pillared layered silicates and host layered silicates.

Samples	S_{BET} (m^2/g)	V_{tot}(ml/g)	V_{micro}(ml/g)
Na-Mica	9	0.03	-
Kunipia-G	5	0.01	-
TM-500	242 (0.999)	0.21	0.10
TK-500	314 (0.999)	0.25	0.14
TFeM-500	347 (0.997)	0.27	0.15
TMgM-300	299 (0.998)	0.25	0.12
TMgM-400	376 (0.997)	0.30	0.16
TMgM-500	335 (0.997)	0.29	0.15
TMgM-600	266 (0.998)	0.26	0.11.
TMgM-700	250 (0.999)	0.26	0.10
TMgM-800	16 (1.000)	0.10	-

*S_{BET} : BET specific surface area, V_{tot} : total volume, V_{micro} : micropore volume calculated by t-plot. The value in ( ) is a correlation factor of BET equation.

Table S3. Results of nonlinear least-squares curve-fitting analysis for the Ti K-edge EXAFS spectra of TiO$_2$-Pillared clays and anatase TiO$_2$.

| Samples	Bond	CN	R	ΔE_0	σ^2
	Ti–O	6.0	1.95	0.51	4.9
Anatase TiO$_2$	Ti–Ti$_{edge}$	4.0	3.04	-0.47	5.1
	Ti–Ti$_{corner}$	4.0	3.79	1.12	6.3
	Ti–O	5.6	1.96	4.42	6.1
TM-500	Ti–Ti$_{edge}$	2.4	3.05	3.08	6.8
	Ti–Ti$_{corner}$	2.6	3.84	3.28	7.8
	Ti–O	5.7	1.98	4.91	6.9
TMgM-500	Ti–Ti$_{edge}$	3.0	3.07	-0.38	9.9
	Ti–Ti$_{corner}$	2.9	3.85	1.47	10.3
	Ti–O	5.5	1.97	4.78	6.8
TFeM-500	Ti–Ti$_{edge}$	2.9	3.03	0.30	9.1
	Ti–Ti$_{corner}$	3.0	3.80	2.71	8.4

*The fitting range for k is 2.62-12.90 Å^{-1}, and that for R is 1.00-3.85 Å. Errors in CN (coordination number) and σ^2 (Debye-Waller factor, 10^{-3} Å^2) are 20%, and those in R (interatomic distance) and ΔE_0 (threshold energy difference) are 0.02 Å and 2.0 eV, respectively.

Scheme S1
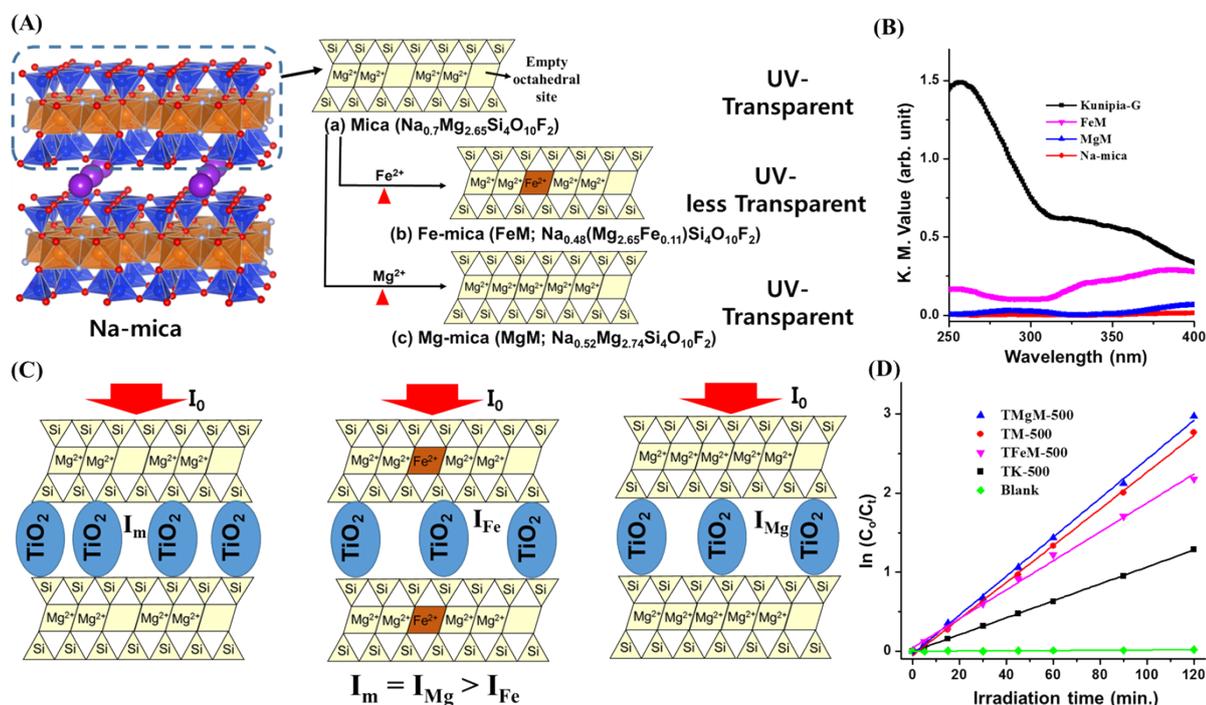
Scheme S1. (A) Structure of Na-mica and modified micas (FeM and MgM), (B) UV-vis spectra of Na-mica, modified micas and Kunipia-F (natural montmorillonites), (C) their schematic TiO_2 pillared structures and (D) time-dependent curves of the concentration of methyl orange (MO) upon photocatalytic degradation reaction under UV irradiation ($\lambda > 290$ nm) with and without TiO_2 pillared clays.

Fig. S1.
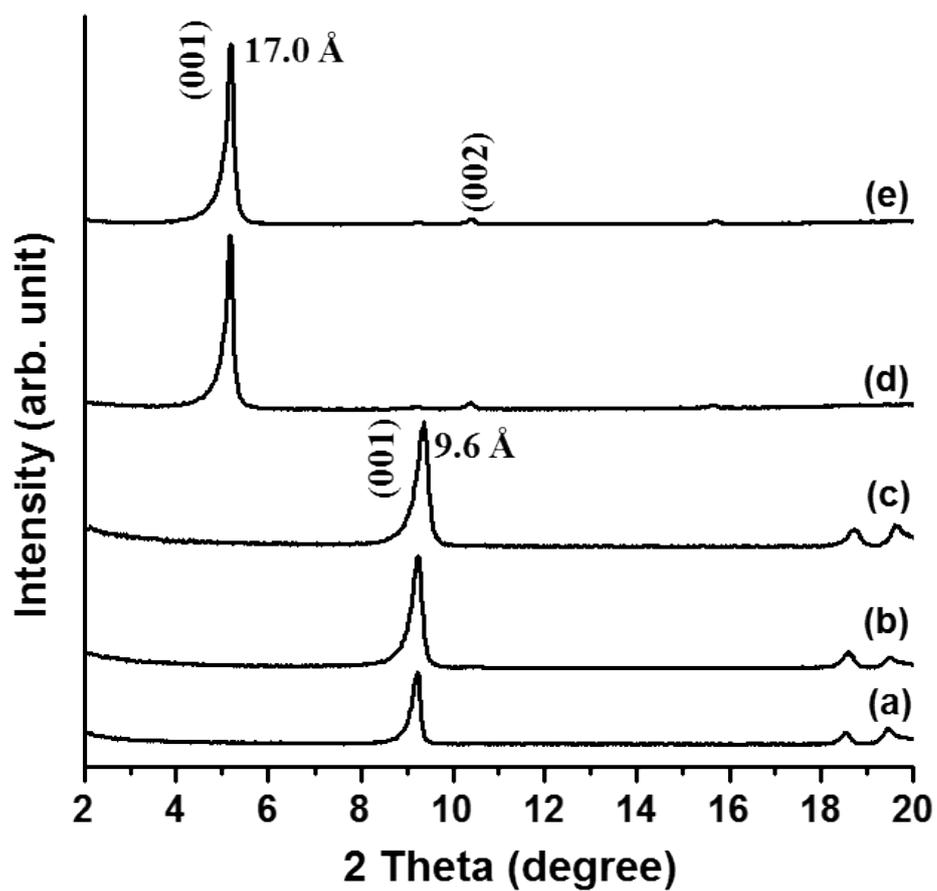
Fig. S1 X-ray diffraction patterns of (a) Na-mica, (b) Mg^{2+} modified Na-mica (MgM), (c) Fe^{2+} modified Na-mica (FeM), (d) ethylene glycol (EG) intercalated MgM and (e) EG intercalated FeM.
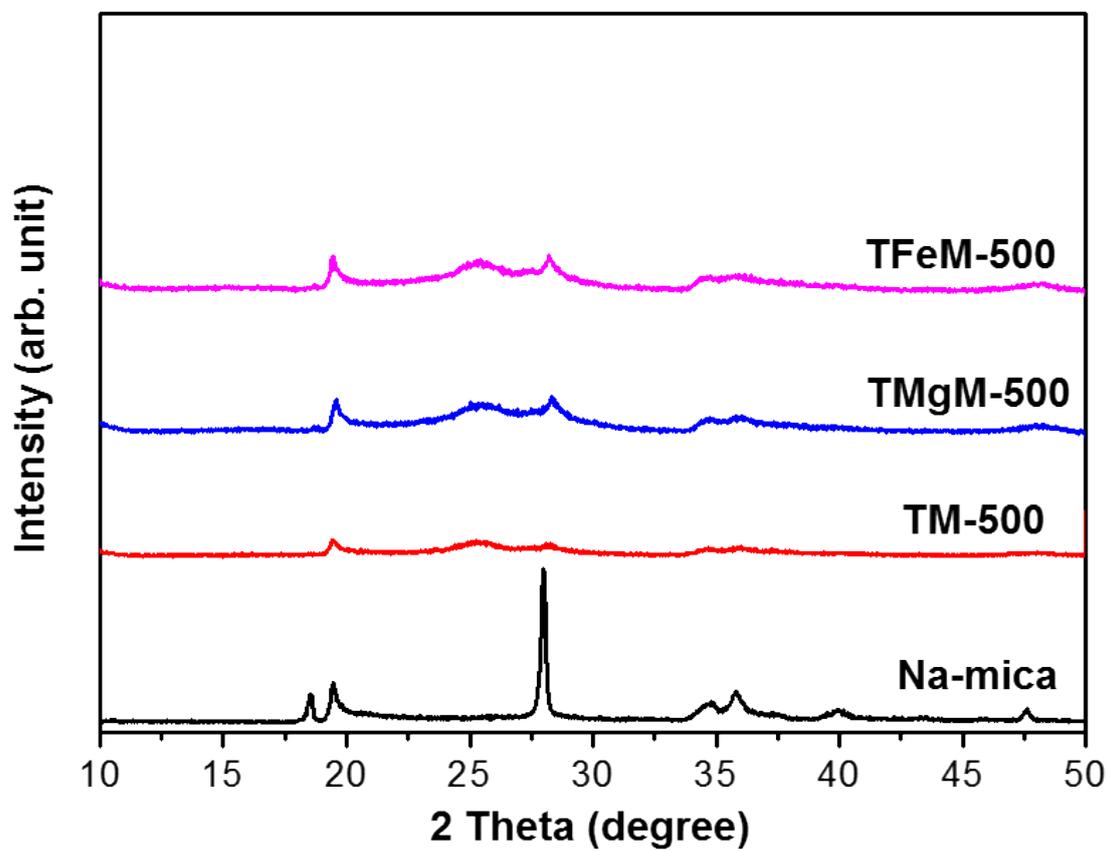
Fig. S2 Wide angle X-ray diffraction patterns of (a) Na-mica, (b) TM-500, (c) TMgM-500 and (d) TFeM-500.