Supplementary materials

Photocatalytic Activity and Stability of Organically Modified Layered Perovskite-Like Titanates $HLnTiO_4$ (Ln = La, Nd) in the Reaction of Hydrogen Evolution from Aqueous Methanol

Sergei A. Kurnosenko, Vladimir V. Voytovich, Oleg I. Silyukov, Ivan A. Rodionov and Irina A. Zvereva *

Department of Chemical Thermodynamics and Kinetics, Institute of Chemistry, Saint Petersburg State University, Saint Petersburg 199034, Russia; st040572@student.spbu.ru (S.A.K.); st062003@student.spbu.ru (V.V.V.); oleg.silyukov@spbu.ru (O.I.S.); i.rodionov@spbu.ru (I.A.R.)
* Correspondence: irina.zvereva@spbu.ru

Information S1

Method for calculation of apparent quantum efficiency

Apparent quantum efficiency φ of photocatalytic hydrogen generation was calculated using the following formula (S1):

$$\varphi = \frac{2\omega}{f} \cdot 100\% \qquad \text{(S1)}$$

where ω is the hydrogen evolution rate (mmol/h) and f is the photon flux in the photocatalyst absorption range (mmol/h).

The photon flux was measured previously in accordance with the conventional ferrioxalate actinometry technique. Briefly, 3 g of potassium ferrioxalate $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ was dissolved in 1000 ml of 0.05 M sulfuric acid. 50 ml of the photosensitive solution prepared was pumped into the reaction compartment of the photocatalytic cell and irradiated by the DRT-125 lamp through the NaBr + KCl light filter (transmission range $\lambda > 220$ nm) for 20 s. Then 0.5 ml of the irradiated solution was sampled from the cell, mixed with 2 ml of an acetate buffer and 1 ml of 0.1% 1,10-phenanthroline and made up to the 25 ml mark with distilled water in a volumetric flask. Amount of Fe^{2+} in the final solution was determined spectrophotometrically using a previously built calibration plot. The similar experiment was conducted using a KNO_3 light filter and irradiation time 30 s (transmission range $\lambda > 340$ nm). Each series of measurements was repeated 3 times and Fe^{2+} contents were averaged. Assuming the quantum yield of the Fe^{2+} formation from potassium ferrioxalate is 100%, we calculated the photon flux f in the active range (220–340 nm) in accordance with the formula (S2):

$$f = V \cdot \left(\frac{c}{t} - \frac{c'}{t'}\right) \qquad \text{(S2)}$$

where V is a volume of the photosensitive solution in the cell (l), c is concentration of Fe^{2+} (mM) in the photosensitive solution after its irradiation through the NaBr + KCl light filter for the time t (h), c' is concentration of Fe^{2+} (mM) in the photosensitive solution after its irradiation through the KNO_3 light filter for the time t' (h).

Figure S1

XRD patterns of the initial protonated titanates HLT and HNT and their inorganic-organic derivatives

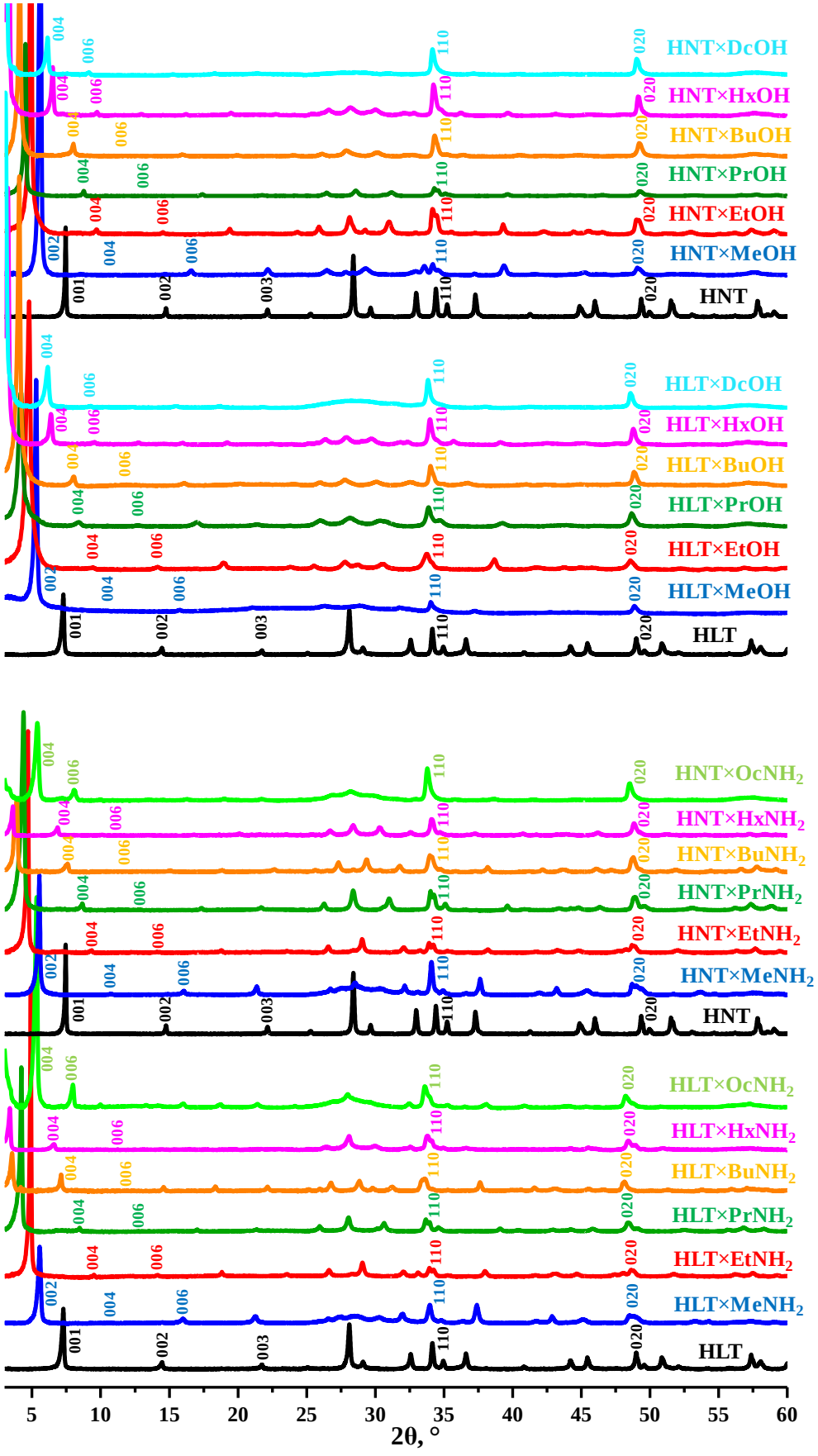


Figure S2

Diffuse reflectance spectra and Tauc plots for the initial protonated titanates HLT (a) and HNT (b)

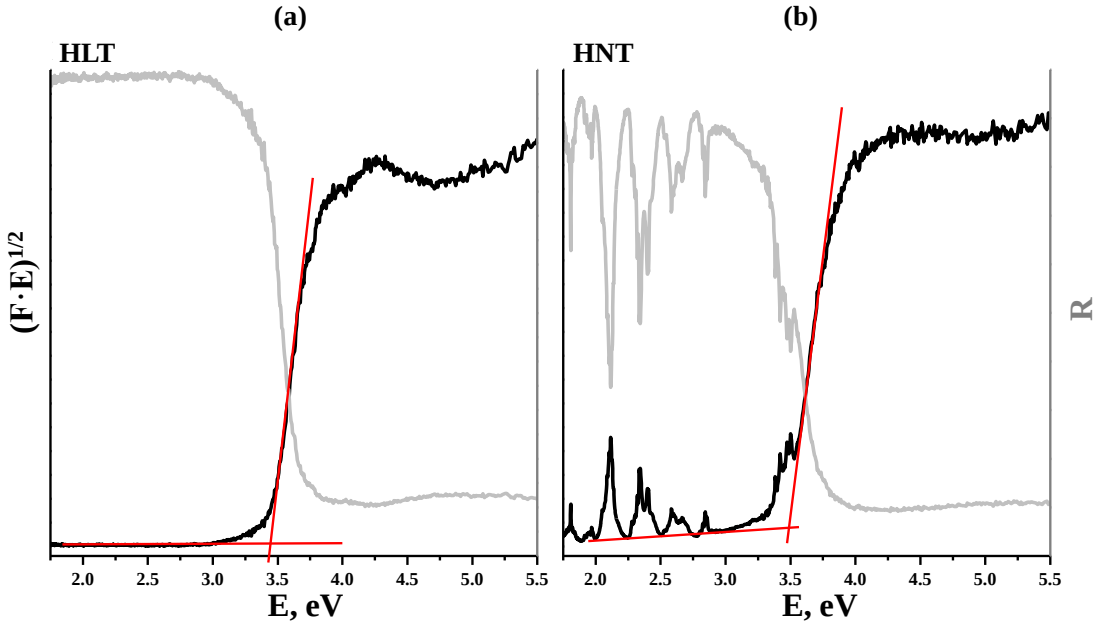


Figure S3

Diffuse reflectance spectra and Tauc plots for *n*-alkylamine (a) and *n*-alkoxy (b) derivatives of HLT and HNT

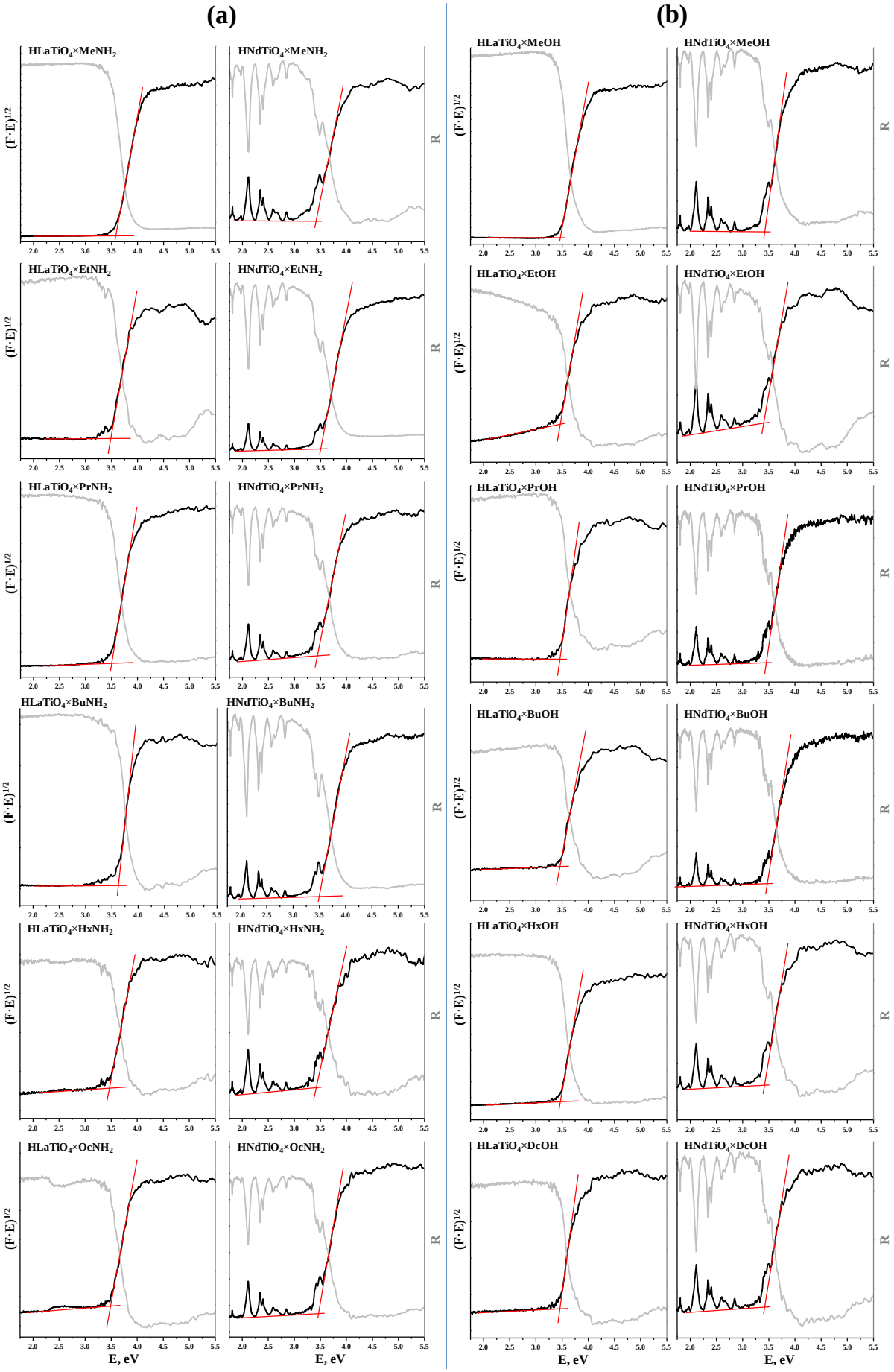


Figure S4

Emission spectrum of the DRT-125 lamp and absorption regions of the samples under study

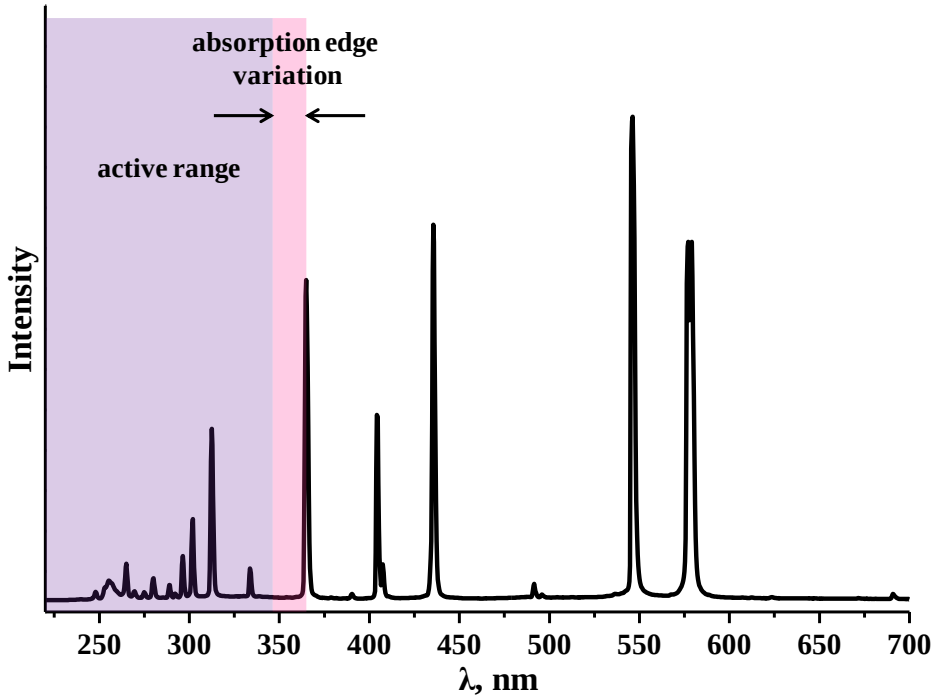


Figure S5

Comparison of actual volume concentrations of the HLT- (a, b) and HNT-based (c, d) samples in reaction suspensions in the beginning and in the ending of the photocatalytic experiment

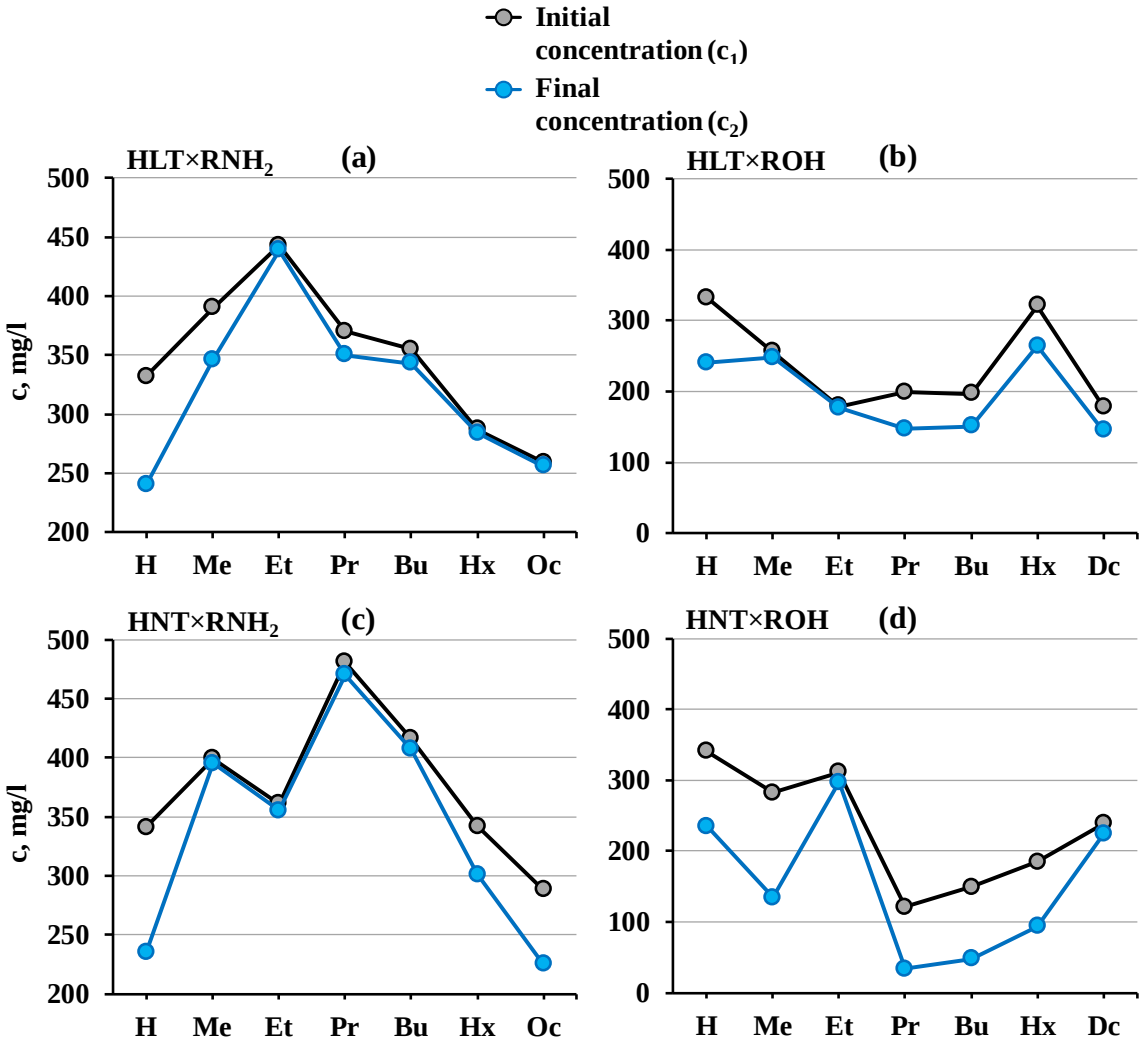


Figure S6

Hydrogen generation rate from 1 mol. % aqueous methanol over platinized ethylamine (a) and methoxy (b) derivatives of HLT after several running cycles

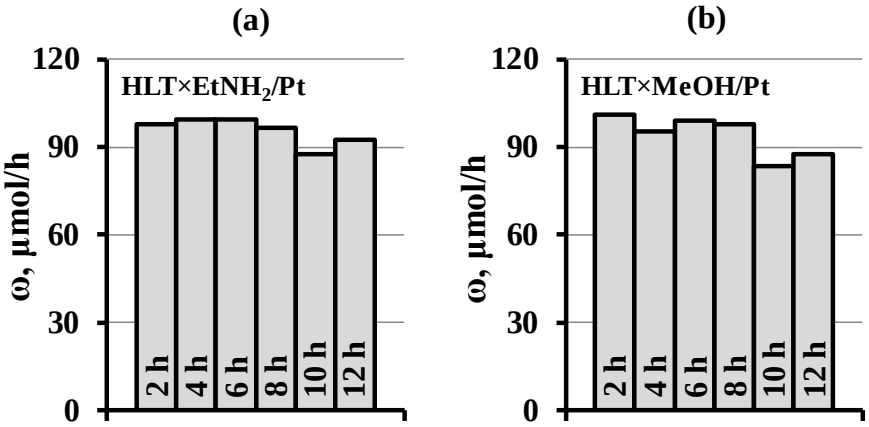


Figure S7

TG curves of methylamine (a), ethylamine (b), *n*-octylamine (c), methoxy (d) and *n*-decoxy (e) derivatives of HLT before and after photocatalytic (PC) experiments

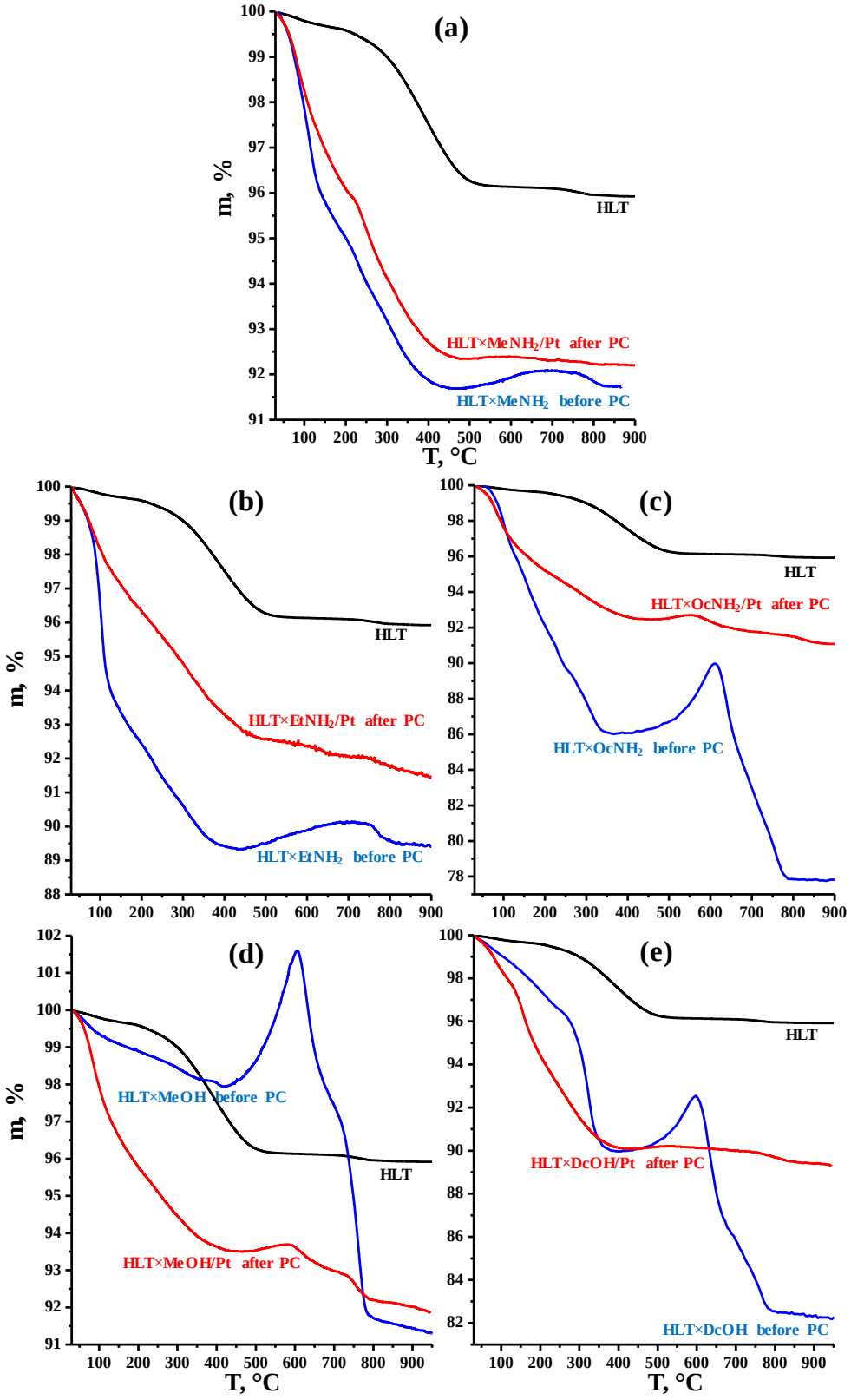
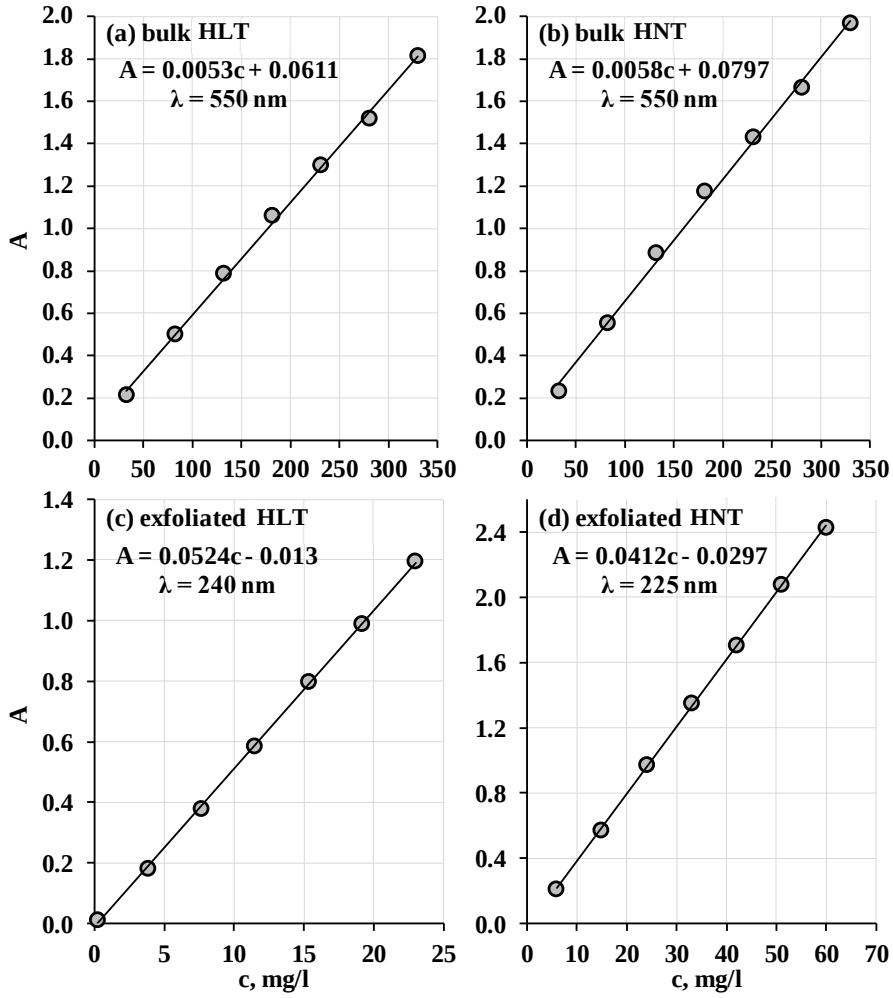


Figure S8

Spectrophotometric calibration plots for monitoring the volume concentrations of bulk (a, b) and exfoliated (c, d) fractions and HLT- and HNT-based samples in the reaction suspensions

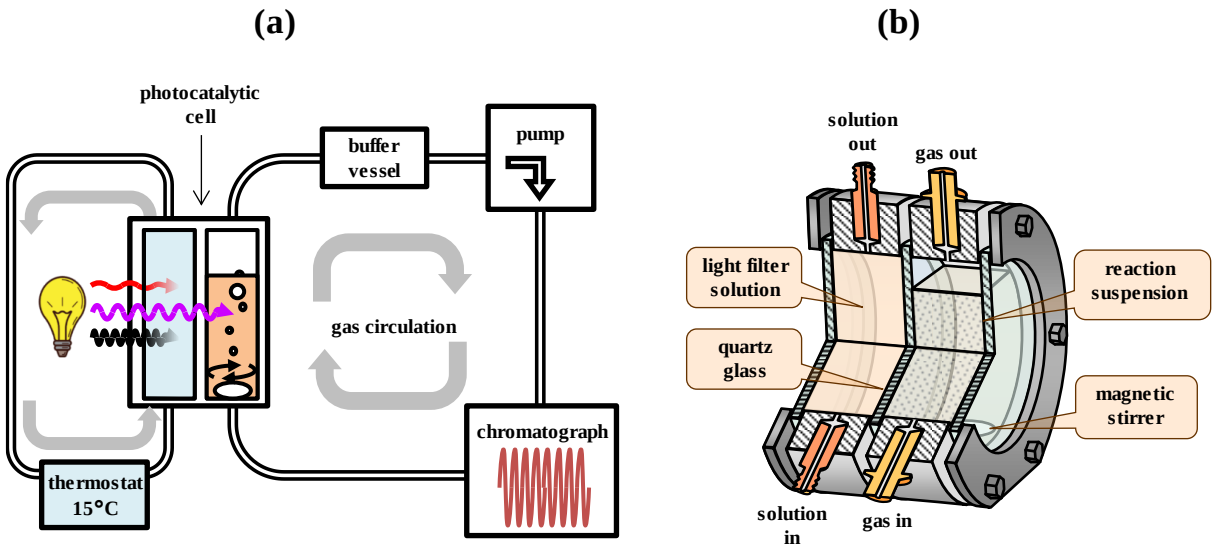


To prepare the calibration plot for suspensions of bulk non-exfoliated titanates for the determination of c_1 and c_2 concentrations during photocatalytic experiments, a hitch of each methylamine derivative HLT×$MeNH_2$ (HNT×$MeNH_2$), containing by calculation 0.03 g of the inorganic component (excluding intercalated water) was added to 60 ml of 1 mol. % methanol. Then the mixture was sonicated for 10 min in an Elmasonic S10H bath (Elma, Singen, Germany). Afterwards, the suspension obtained was used to build the spectrophotometric calibration dependence in coordinates optical density (A) – titanate concentration in mg/l (c). For this, a series of spectra with various suspension dilutions was recorded, analytical wavelength λ = 550 nm was selected and linear approximation of the experimental dependence $A_\lambda = A_\lambda$ (c) was found using the least-squares method (graphs a, b).

To prepare the calibration plot for suspensions of titanate nanosheets for the determination of c_3 concentration after photocatalytic experiments, a hitch of each methylamine derivative HLT×$MeNH_2$ (HNT×$MeNH_2$), containing by calculation 0.03 g of the inorganic component (excluding intercalated water) was placed into a glass tube with 30 ml of 0.004 M aqueous tetrabutylammonium hydroxide (TBAOH) and sonicated by a Hielscher UP200St homogenizer (Teltow, Germany) at a half power for 5 min. After shaking at room temperature for 24 h, the suspension was sonicated for 5 min again. Hereafter bulk non-exfoliated particles were separated via centrifuging at a separation factor F = 1000 for 1 h and concentration of the colloidal solution obtained was determined by ICP-AES after preliminary acid digestion. To obtain the calibration plot A – c (mg/l), a series of spectra with various suspension dilutions was recorded, analytical wavelength λ = 240 nm (Ln = La) or λ = 225 nm (Ln = Nd) was selected and linear approximation of the experimental dependence $A_\lambda = A_\lambda$ (c) was found using the least-squares method (graphs c, d).

Scheme S1

Scheme of photocatalytic setting (a) and reaction cell (b) and their operating principle



Photocatalytic measurements were performed on the laboratory photocatalytic setting, consisting of an illuminator, reaction cell, online gas chromatograph and closed gas circulation system, connecting the last two components. An arc mercury tube lamp DRT-125 (125 W) serves as an ultraviolet irradiation source providing a photon flux of 14.96 mmol/h in the range of the photocatalysts' absorption (spectrum in shown in Supporting Information S4). The self-made photocatalytic cell represents an external irradiation reactor, including two compartments equipped with branch pipes for the supply and removal of solutions and gases. The compartment closest to the lamp is filled with an aqueous solution of NaBr and KCl (6 g/l of each salt) serving as a light filter. The latter allows cutting of hard ultraviolet irradiation ($\lambda < 220$ nm) as well as provides cooling of the cell, which is achieved by its continuous circulation through the thermostat, connected to the cold-water system and maintaining a temperature of 15 °C. The compartment farthest from the lamp is for the reaction suspension being intensively stirred during the experiment. Gaseous reaction products come from the cell into the gas circulation system. Their detection is conducted according to a specified program at fixed time intervals by a Shimadzu GC-2014 gas chromatograph (Kyoto, Japan), equipped with a 30 m long Rt-Msieve 5A capillary column, thermal conductivity detector and using argon as a carrier gas.

Table S1

Photocatalytic activity of the initial protonated titanates and their inorganic-organic derivatives in a bare form and after surface modification with a Pt cocatalyst

Sample	ω, μmol/h	φ, %	k_{Pt}	Sample	ω, μmol/h	φ, %	k_{Pt}
HLT	0.73	0.01	19	HNT	0.73	0.01	8
HLT/Pt	14	0.19		HNT/Pt	6.2	0.08	
HLT×$MeNH_2$	23	0.31	2	HNT×$MeNH_2$	1.1	0.014	15
HLT×$MeNH_2$/Pt	48	0.65		HNT×$MeNH_2$/Pt	16	0.22	
HLT×$EtNH_2$	8.2	0.11	12	HNT×$EtNH_2$	1.1	0.015	10
HLT×$EtNH_2$/Pt	98	1.3		HNT×$EtNH_2$/Pt	11	0.15	
HLT×$PrNH_2$	7.4	0.10	9	HNT×$PrNH_2$	2.2	0.03	10
HLT×$PrNH_2$/Pt	70	0.93		HNT×$PrNH_2$/Pt	23	0.31	
HLT×$BuNH_2$	13	0.17	4	HNT×$BuNH_2$	1.1	0.015	11
HLT×$BuNH_2$/Pt	57	0.76		HNT×$BuNH_2$/Pt	12	0.16	
HLT×$HxNH_2$	15	0.20	6	HNT×$HxNH_2$	1.1	0.015	20
HLT×$HxNH_2$/Pt	91	1.2		HNT×$HxNH_2$/Pt	22	0.30	
HLT×$OcNH_2$	18	0.24	4	HNT×$OcNH_2$	1.1	0.015	25
HLT×$OcNH_2$/Pt	72	0.96		HNT×$OcNH_2$/Pt	28	0.38	
HLT×MeOH	50	0.67	2	HNT×MeOH	13	0.17	3
HLT×MeOH/Pt	100	1.4		HNT×MeOH/Pt	40	0.54	
HLT×EtOH	13	0.18	3	HNT×EtOH	6.7	0.09	2
HLT×EtOH/Pt	38	0.50		HNT×EtOH/Pt	16	0.22	
HLT×PrOH	4.9	0.07	12	HNT×PrOH	3.3	0.04	11
HLT×PrOH/Pt	59	0.80		HNT×PrOH/Pt	35	0.46	
HLT×BuOH	5.1	0.07	10	HNT×BuOH	3.0	0.04	9
HLT×BuOH/Pt	53	0.70		HNT×BuOH/Pt	27	0.36	
HLT×HxOH	2.9	0.04	16	HNT×HxOH	1.5	0.02	14
HLT×HxOH/Pt	47	0.63		HNT×HxOH/Pt	21	0.28	
HLT×DcOH	3.3	0.04	8	HNT×DcOH	9.3	0.12	4
HLT×DcOH/Pt	25	0.33		HNT×DcOH/Pt	35	0.47	

Table S2

Actual volume concentrations and pH values of the reaction suspensions of HLT-based samples (c_1, pH_1 – at the beginning of the photocatalytic experiment; c_2, pH_2 – at the ending; c_3, pH_3 – after centrifuging)

Photocatalyst	**c_1, mg/l**	**c_2, mg/l**	**c_3, mg/l**	**pH_1**	**pH_2**	**pH_3**
HLT	332	239	1.6	6.4	6.3	6.3
HLT/Pt	205	98.4	–	4.6	4.6	4.5
HLT×$MeNH_2$	390	346	0.9	9.4	9.2	9.3
HLT×$MeNH_2$/Pt	344	339	–	8.0	6.6	6.8
HLT×$EtNH_2$	443	439	0.9	9.3	9.6	9.5
HLT×$EtNH_2$/Pt	407	261	–	7.7	5.7	6.5
HLT×$PrNH_2$	370	350	0.5	8.7	8.4	8.5
HLT×$PrNH_2$/Pt	418	410	–	7.7	6.6	6.9
HLT×$BuNH_2$	355	343	1.0	8.5	8.2	8.8
HLT×$BuNH_2$/Pt	320	177	–	7.2	5.3	5.5
HLT×$HxNH_2$	287	284	0.4	8.7	8.7	9.0
HLT×$HxNH_2$/Pt	258	139	–	7.3	5.9	5.8
HLT×$OcNH_2$	259	256	0.5	7.6	7.7	7.8
HLT×$OcNH_2$/Pt	194	154	–	7.1	6.3	6.2
HLT×MeOH	256	248	0.2	4.8	4.3	4.2
HLT×MeOH/Pt	174	169	–	4.2	4.1	4.3
HLT×EtOH	179	177	0.2	6.1	5.5	6.0
HLT×EtOH/Pt	157	114	–	5.2	6.2	6.2
HLT×PrOH	199	147	0.3	6.0	6.4	6.1
HLT×PrOH/Pt	203	76.2	–	4.7	5.9	6.0
HLT×BuOH	197	151	0.4	4.5	5.6	5.7
HLT×BuOH/Pt	127	59.1	–	4.7	5.6	5.8
HLT×HxOH	321	264	0.4	5.7	6.1	6.1
HLT×HxOH/Pt	187	144	–	5.5	6.1	6.1
HLT×DcOH	178	145	0.2	5.3	5.5	5.5
HLT×DcOH/Pt	188	62.8	–	5.0	6.2	6.1

Table S3

Actual volume concentrations and pH values of the reaction suspensions of HNT-based samples (c_1, pH_1 – at the beginning of the photocatalytic experiment; c_2, pH_2 – at the ending; c_3, pH_3 – after centrifuging)

Photocatalyst	**c_1, mg/l**	**c_2, mg/l**	**c_3, mg/l**	**pH_1**	**pH_2**	**pH_3**
HNT	341	235	1.0	6.3	6.1	5.9
HNT/Pt	142	85.0	–	4.7	4.5	4.4
HNT×$MeNH_2$	399	395	1.7	9.9	9.9	10
HNT×$MeNH_2$/Pt	356	340	–	8.6	7.9	7.9
HNT×$EtNH_2$	361	355	6.6	9.8	9.9	9.9
HNT×$EtNH_2$/Pt	431	373	–	8.7	8.2	7.6
HNT×$PrNH_2$	481	470	4.3	9.5	9.2	9.3
HNT×$PrNH_2$/Pt	494	487	–	8.5	7.8	7.9
HNT×$BuNH_2$	416	407	1.9	9.5	9.4	9.5
HNT×$BuNH_2$/Pt	409	403	–	7.9	7.2	6.9
HNT×$HxNH_2$	342	301	1.7	9.1	9.2	9.4
HNT×$HxNH_2$/Pt	273	258	–	7.8	7.3	7.5
HNT×$OcNH_2$	288	225	0.9	7.8	8.2	8.2
HNT×$OcNH_2$/Pt	218	210	–	7.1	7.0	7.0
HNT×MeOH	282	134	0.8	5.8	4.8	4.8
HNT×MeOH/Pt	174	77.4	–	4.7	4.4	4.4
HNT×EtOH	311	297	0.6	6.2	5.7	5.6
HNT×EtOH/Pt	215	142	–	4.9	5.1	5.1
HNT×PrOH	121	33.6	0.6	6.0	6.3	5.9
HNT×PrOH/Pt	99.9	53.4	–	4.5	4.4	4.5
HNT×BuOH	149	47.8	1.5	5.5	5.6	5.7
HNT×BuOH/Pt	94.6	75.7	–	4.3	4.5	4.6
HNT×HxOH	185	93.9	0.7	5.5	5.8	5.8
HNT×HxOH/Pt	123	115	–	4.6	4.9	4.8
HNT×DcOH	239	224	1.1	5.5	4.9	4.9
HNT×DcOH/Pt	163	163	–	4.5	4.4	4.4

Table S4

Conditions for synthesis of the initial titanates and their inorganic-organic derivatives. Here abbreviations NLT, HLT refer to both La- and Nd-containing samples

	Sample	**Precursors used**	**Reaction solution**	**Temperature, °C**	**Duration, d**
	NLT	TiO_2, Ln_2O_3, Na_2CO_3	–	825	0.5
	HLT	NLT	0.1 M aq. HCl	25	1
n-alkylamine derivatives	HLT×$MeNH_2$	HLT	38% aq. $MeNH_2$	60	10
	HLT×$EtNH_2$	HLT×$MeNH_2$	70% aq. $EtNH_2$	25	1
	HLT×$PrNH_2$		90% aq. $PrNH_2$		
	HLT×$BuNH_2$		90% aq. $BuNH_2$		
	HLT×$HxNH_2$		30% $HxNH_2$ in *n*-heptane	60	7
	HLT×$OcNH_2$		30% $OcNH_2$ in *n*-heptane		
n-alkoxy derivatives	HLT×MeOH	HLT×$MeNH_2$	100% MeOH	100	7
	HLT×EtOH		96% aq. EtOH		
	HLT×PrOH	HLT×$BuNH_2$	100% PrOH	180	
	HLT×BuOH		100% BuOH		
	HLT×HxOH		100% HxOH		
	HLT×DcOH		30% DcOH in *n*-heptane		10