

Electronic Supplementary Information

Titanate nanosheets as highly efficient non-light-driven catalysts for degradation of organic dyes

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Experimental section

1. Catalyst preparation

The titanate nanosheets (TNSs) colloid was achieved according to the delamination approach described in our previous work.¹⁻⁵ Typically, the precursor layered titanate of $K_{0.8}Ti_{1.73}Li_{0.27}O_4$ was synthesized by solid-state calcination of a mixture of stoichiometric Li_2CO_3 , K_2CO_3 , and TiO_2 at 1000 °C. It was converted into its protonic titanate, $H_{1.07}Ti_{1.73}O_4 \cdot H_2O$ (denoted as LPT), by repeating acid-exchange 3 times using a 1 M HCl solution. Then, 1 g of LPT powder was dispersed into an ethylamine aqueous solution (0.025 M, 250 mL) and the mixture was shaken for 24 h, which resulted in the delamination of LPT into unilamellar TNSs colloid. The dispersed TNSs were immediately aggregated as soon as an HCl aqueous solution was added in drop by drop. Finally, the restacked TNSs, designated as rs-TNSs, was collected by centrifugation, water-washed to remove redundant HCl and dried at 70 °C over night.

2. Characterization

Atomic Force Microscope (AFM) image was acquired in height mode using a MultiMode-8 scanning probe microscope (Bruker Co. Ltd. USA). The sample was prepared by drop-casting corresponding dilute dispersions onto freshly cleaved silicon slice surface. A scanning electron microscope (SEM, Hitachi S-4800) was used to observe the morphology of catalysts.

Transmission electron microscope (TEM) images were taken on a JEOL-2100 electron microscope operating at an accelerating voltage of 200 kV. The specific surface area of sample was deduced by the BET method (N₂ adsorption) with a Micromeritics ASAP 2020 system. Powder X-ray diffraction (XRD) patterns of samples were collected on a DX-2700 diffractometer (Dandong Haoyuan Instrument Co. Ltd) using Cu K α radiation. UV-vis absorption spectra and diffuse-reflectance spectra were performed on a Shimadzu UV-2450 spectrophotometer using BaSO₄ as the reference. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos AXIS Ultra DLD instrument with an Al K α monochromatic source. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Avatar 370 spectrophotometer using the standard KBr disk method.

3. Non-light-driven catalysis for degradation of organic dyes

All the experiments were carried out in a lightproof box covered with aluminum foil at room temperature. In a typical run, a given amount of rs-TNSs was added into 50 mL of RhB solution with a desired pH value, which was carefully adjusted by a NaOH or HCl solution (the initial pH of RhB solution without adjusting was 4.5). Prior to the reaction, the mixture was magnetically stirred for 60 min to establish the adsorption/desorption equilibrium. The non-light-driven catalysis was initiated by adding a known concentration of H₂O₂ solution to the above suspension with continuous stirring. At the given time intervals, 3 mL of the mixture were sampled and then these samples were analyzed immediately after separating catalyst particles by centrifugation. The absorption spectrum of RhB solution was measured on a Shimadzu UV-2450 spectrophotometer. The degradation efficiency of RhB was obtained by calculating the change of concentration (C/C_0) from the variation of absorbance (A/A_0) at 554 nm. C_0 and A_0 denote the concentration and absorbance of RhB solution after stirring the suspension for 60 min. The reaction kinetics of non-light-driven catalytic degradation of dyes was studied using the first-order kinetics equation: $\ln(C/C_0) = -kt$, where k is the rate constant (k). The intermediates in this catalysis reaction were checked by an external standard method in high performance liquid chromatography (HPLC, Shimadzu; pump: Essentia LC-15C; detector: SPD-15C; column: WondaSil C18, 4.6 \times 150 mm, 0.5 μ m; flow: 0.8 mL min⁻¹, V(CH₃OH/H₂O) = 0.8). The H₂O₂ concentration and the COD value were detected by a KMnO₄ titration method.

1. Y. Tian, J. Fu, B. Chang, F. Xi and X. Dong, Mater. Lett., 2012, **81**, 95.

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2. J. Fu, Y. Tian, B. Chang, G. Li, F. Xi and X. Dong, *J. Solid State Chem.*, 2012, **196**, 282.
 3. J. Fu, Y. Tian, B. Chang, F. Xi and X. Dong, *Chem. Eng. J.*, 2013, **219**, 155.
 4. Y. Tian, B. Chang, J. Fu, F. Xi and X. Dong, *Powder Technol.*, 2013, **245**, 227.
 5. J. Luo, Q. Chen and X. Dong, *Powder Technol.*, 2015, **275**, 284.

Table S1 The rate constant (k) of non-light-driven catalytic degradation of RhB by various catalysts.

catalysts	Black	Fe ²⁺		Fe ₂ O ₃	P25	LPT	TNS
		1.0 mg L ⁻¹	10 mg L ⁻¹				
k (10 ⁻³ min ⁻¹)	0.0125	0.53	14.29	0.9657	0.0555	0.0215	23.1

Table S2 The rate constant (k) of non-light-driven catalytic degradation of RhB by rs-TNSs using different H₂O₂ dosage.

H ₂ O ₂ concentration (mg L ⁻¹)	0.00	0.01	0.02	0.06	0.10	0.20
k (min ⁻¹)	0.2053	9.740	11.52	16.81	23.17	28.99

Table S3 The rate constant (k) of non-light-driven catalytic degradation of RhB in varied concentration by rs-TNSs.

RhB concentration (mg L ⁻¹)	5.0	10	15	20	25	30
k (min ⁻¹)	0.0527	0.0307	0.0245	0.0231	0.0241	0.0109

Table S4 The rate constant (k) of non-light-driven catalytic degradation of RhB by rs-TNSs in changed pH value.

pH value	2.8	4.5	7.3	9.2
k (min ⁻¹)	0.0143	0.0231	0.0249	0.0213

Table S5 The retention time (min) of external standards in HPLC and the determined main intermediates in reaction solution with various reaction time.

External standard	1.95	2.31 p-	1.67	2.00	4.52	8.17	6.60
	RhB	HBA	MA	OA	hydroquinone	pyrocatechol	resorcinol
20 min	√	√	√				
40 min	√	√	√				
60 min		√	√				
120 min		√	√	√			
Overnight		√	√				

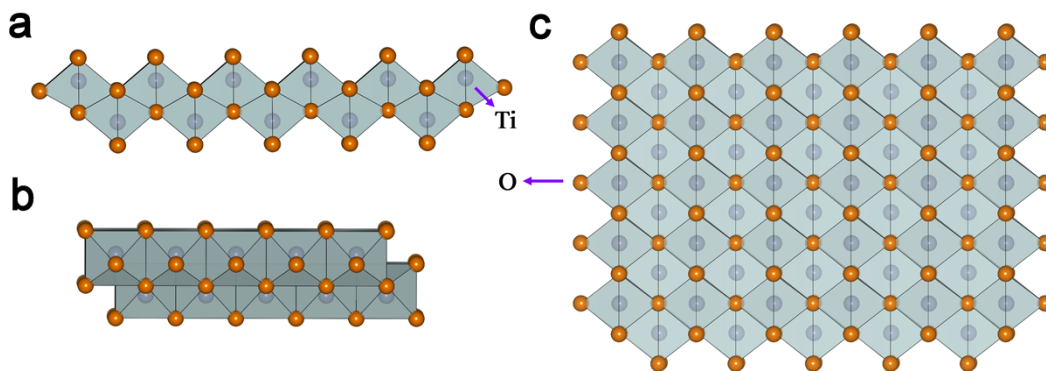


Fig. S1 The structure model of TNSs observed along (a) *c* axes, (b) *a* axes and (c) *b* axes direction.

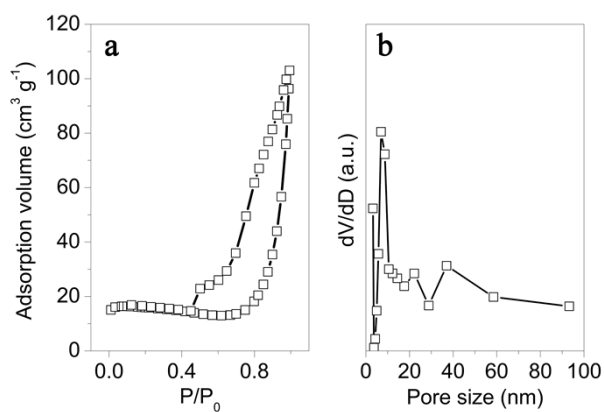


Fig. S2 (a) Nitrogen adsorption-desorption isotherm and (b) its corresponding pore size distribution of rs-TNSs.

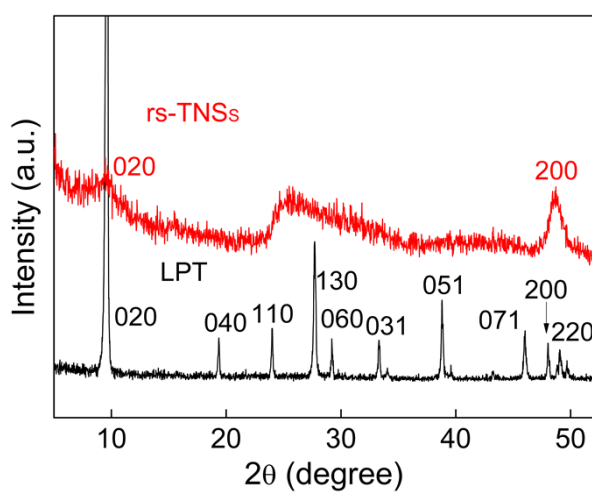


Fig. S3 XRD patterns of LPT and rs-TNSs.

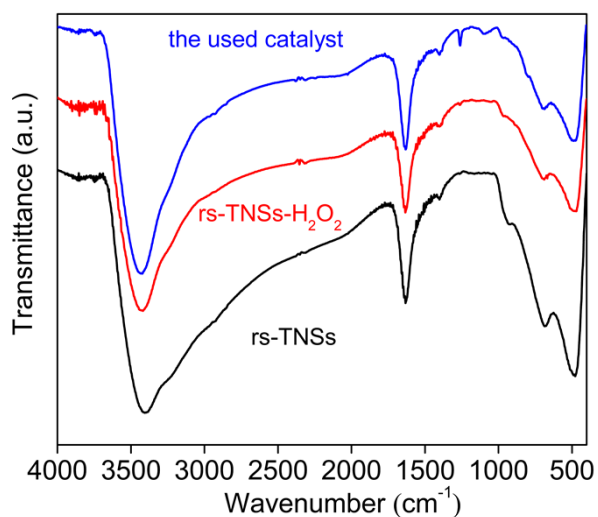


Fig. S4 FTIR spectra of rs-TNSs, rs-TNSs-H₂O₂ and the used catalyst.

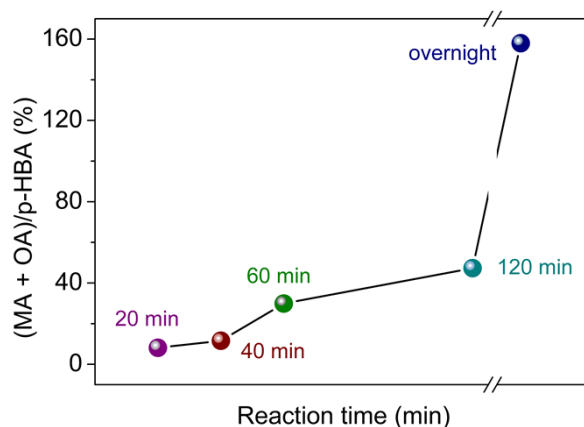


Fig. S5 The variation of (MA + OA)/p-HBA content ratio with the reaction time.

RhB was firstly decomposed to p-HBA, and a p-HBA molecule was further degraded to a MA molecule and an OA molecule. MA can continue to be decomposed to OA that was easily oxidized to CO₂ and H₂O. As a consequence, we only checked OA at the sample of 120 min in HPLC analysis.

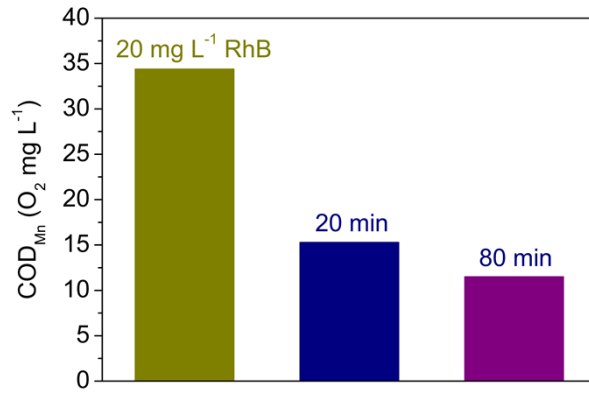


Fig. S6 COD value of reaction solution determined by a KMnO₄ method (the initial H₂O₂ concentration was 0.02 mol L⁻¹). The COD value of initial 20 mg L⁻¹ RhB solution was ~34.4 mg L⁻¹. After 20 min treatment with rs-TNSs, the value was rapidly reduced to ~15.3 mg L⁻¹ and further decreased with the increase of reaction time.

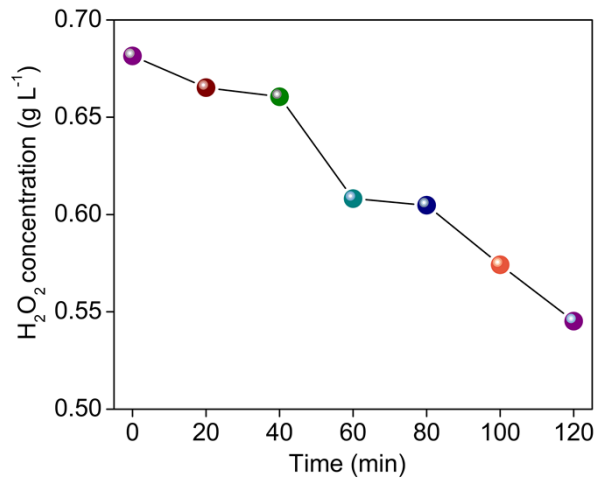


Fig. S7 The change of H₂O₂ concentration with the reaction time (the initial H₂O₂ concentration was 0.02 mol L⁻¹).

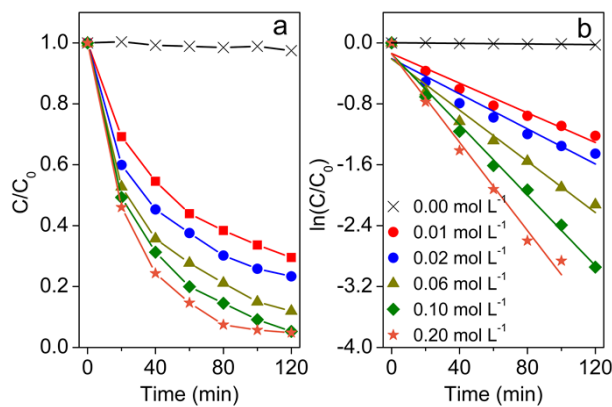


Fig. S8 (a) The non-light-driven catalytic degradation of RhB (20 mg L⁻¹) by rs-TNSs with various H₂O₂ dosage and (b) their corresponding kinetics data.

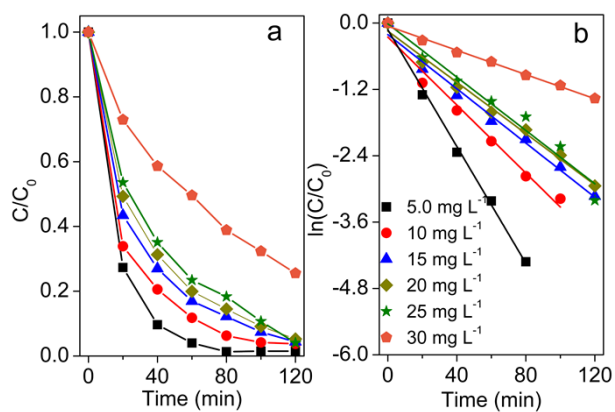


Fig. S9 (a) the non-light-driven catalytic degradation of RhB in different concentration by rs-TNSs with H_2O_2 (0.10 mol L^{-1}) and (b) their corresponding kinetics data.

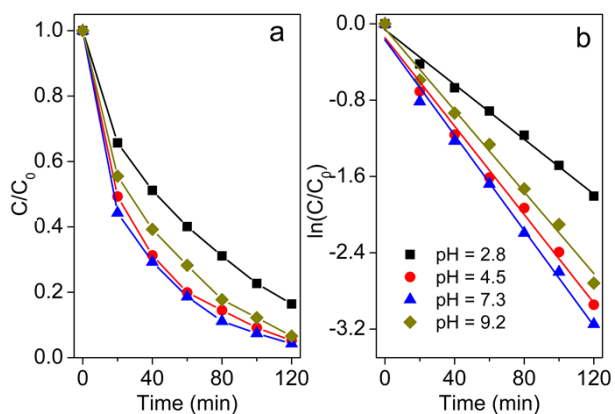


Fig. S10 (a) The non-light-driven catalytic degradation of RhB (20 mg L^{-1}) by rs-TNSs with H_2O_2 (0.10 mol L^{-1}) in changed pH value and (b) their corresponding kinetics data.

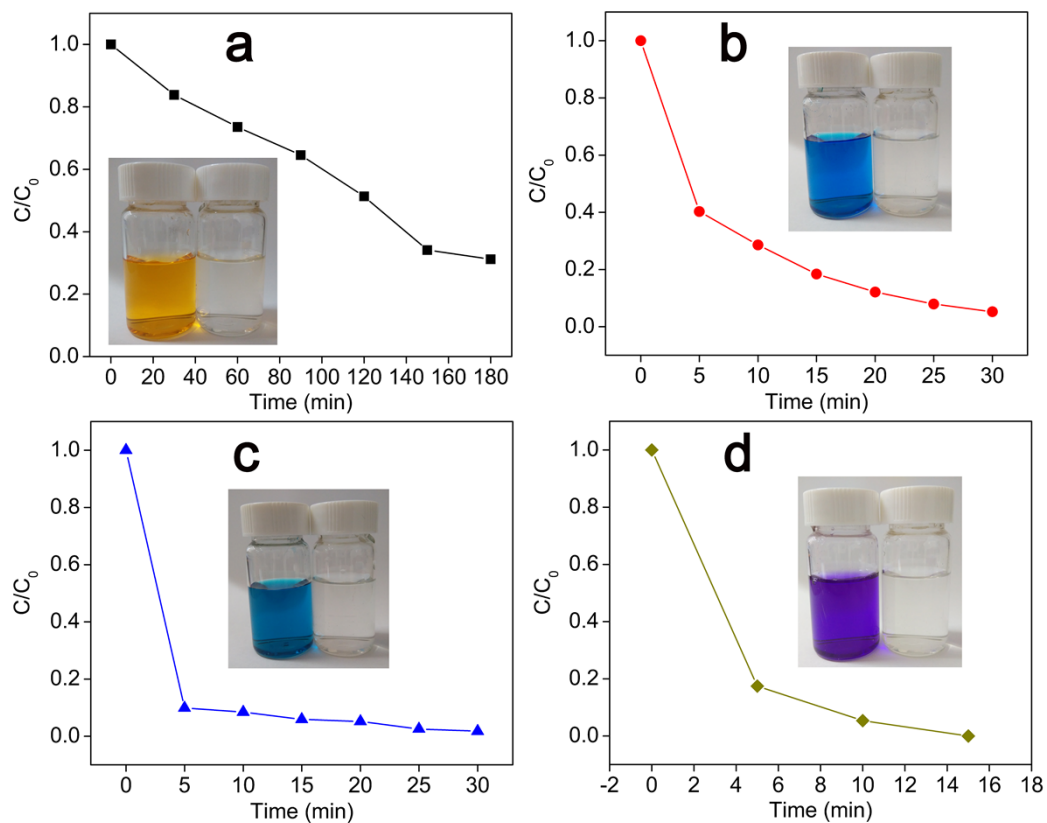


Fig. S11 The non-light-driven catalytic degradation of (a) MO (5 mg L⁻¹), (b) MB (30 mg L⁻¹), (c) MG (30 mg L⁻¹) and (d) MV (30 mg L⁻¹) with a H₂O₂ dosage of 0.10 mol L⁻¹. The insets are corresponding comparisons of dye solution before and after catalytic degradation.