Electronic Supplementary Information

Conductive Nb-doped TiO_2 thin films with the whole visible absorption to degrade pollutants

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1. Simulated Calculation of Electronic Structure of Nb:TiO_2 and TiO_2

Density functional theory (DFT) calculations are employed. A 4×4×2 supercell of TiO_2 with three Nb atoms is used. All calculations are performed using the Vienna Ab-initio Simulation Package (VASP)[1,2] based on generalized gradient approximation with Hubbard U correction (GGA+U)[3] to DFT. Because d orbital plays an important role in transition metals, the U (on-site coulomb term) value for Ti-3*d* is set to be 7 eV, which can give the same band gap (3.2 eV) as experiment of pure TiO_2. The Perdew-Burke-Ernzerhof (PBE) exchange correlation[4] and a plane wave representation for the wave-function with a cut-off of 520 eV are used. The Brillouin zone was sampled by 6×6×3 special k-points using the Monkhorst-Pack scheme for structure optimization, and 12×12×6 for DOS calculation. The calculation will not finish until the force is less than 0.01 eV/Å on each atom and the energy between two successive steps is less than 10^{-4} eV. We consider four different initial configurations of TiO_2-Nb systems and select the configuration which has the lowest energy in electronic structure simulation. The Electronic Structure of TiO_2 was calculated by using a similar process.

Reference:

(1) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54 (16)*, 11169.

(2) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996**, *6 (1)*, 15-50.

(3) Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P. Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1998**, *57(3)*, 1505-1509.

(4) Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1976**, *13 (12)*, 5188-5192.

2. Rietveld Refinement and EDS Data of TiO_2 and NTO Thin Films

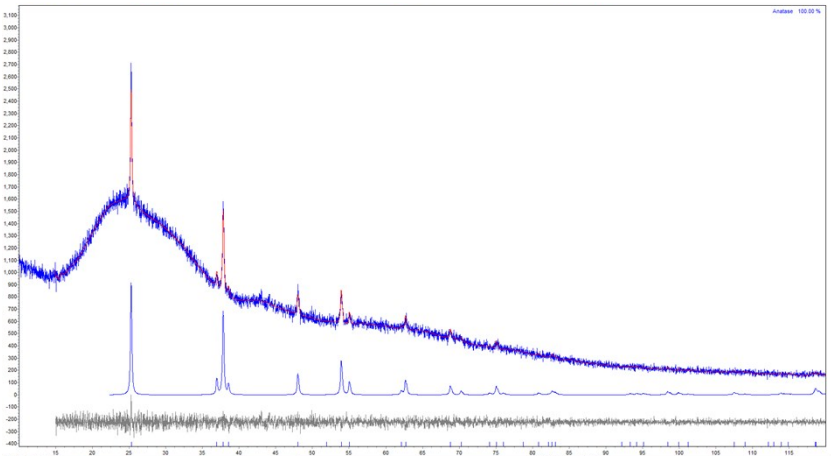

Fig. S1-1 Rietveld refinement profiles: observed (blue solid line), calculated (red solid line), and difference (grey solid line) curve for the fit to the XRD pattern of the thin film TiO_2-RO.

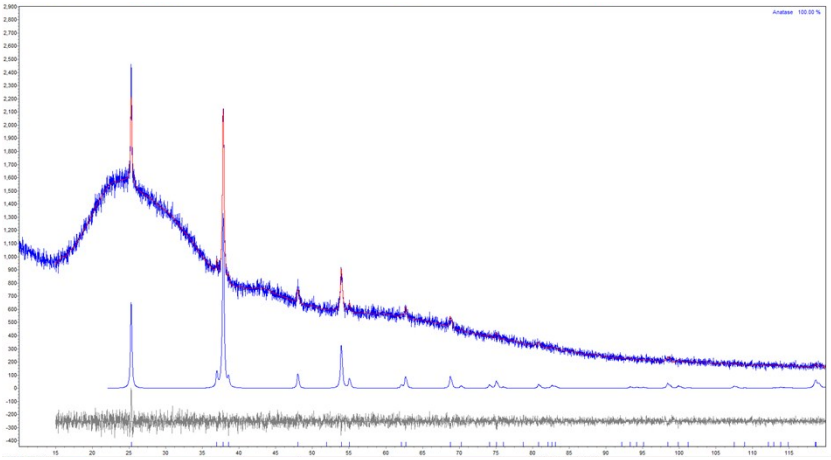

Fig. S1-2 Rietveld refinement profiles: observed (blue solid line), calculated (red solid line), and difference (grey solid line) curve for the fit to the XRD pattern of the thin film TiO_2-004.

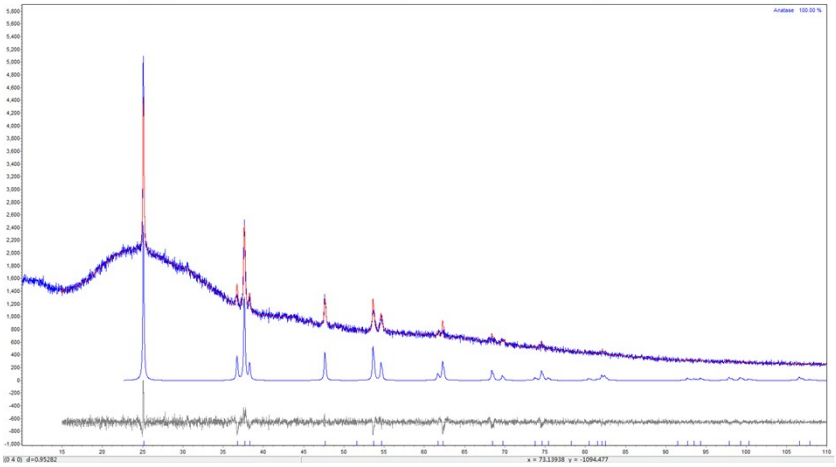

Fig. S1-3 Rietveld refinement profiles: observed (blue solid line), calculated (red solid line), and difference (grey solid line) curve for the fit to the XRD pattern of the thin film NTO-RO.

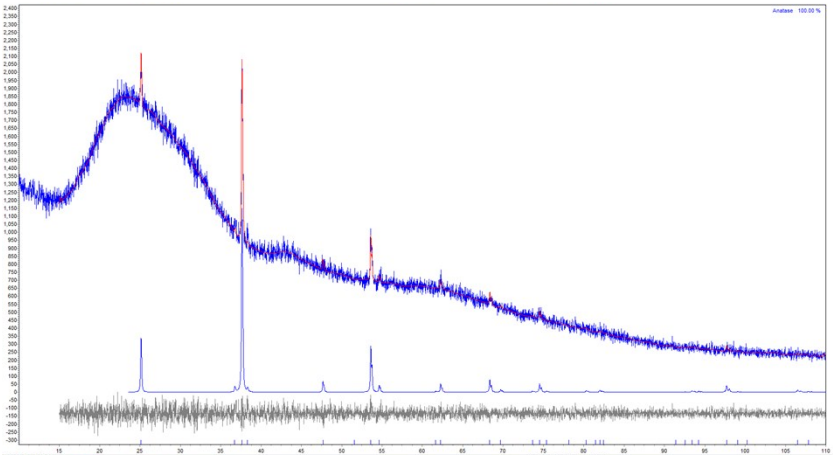

Fig. S1-4 Rietveld refinement profiles: observed (blue solid line), calculated (red solid line), and difference (grey solid line) curve for the fit to the XRD pattern of the thin film NTO-004.

Table S1 Nb:Ti at.% as determined by EDS analysis and lattice parameters of anatase structure for TiO_2 and NTO thin films. Lattice parameters obtained from Le Bail fitting of models to data. The associated fitted R_{wp} for the goodness of fit is given, below 5% indicates a good fit.

Sample number	Nb:Ti by EDS (at. %)	*a* (Å)	*c* (Å)	Unit Cell Volume (Å^3)	Fitted R_{wp} (%)
TiO_2-RO	100 : 0	3.7857(0)	9.5035(3)	136.199(76)	4.1
TiO_2-004	100 : 0	3.7861(0)	9.5042(0)	136.238(29)	4.2
NTO-RO	91.42 : 8.58	3.8113(0)	9.5418(6)	138.605(02)	4.1
NTO-004	91.71 : 8.29	3.8128(6)	9.5577(8)	138.949(94)	3.8

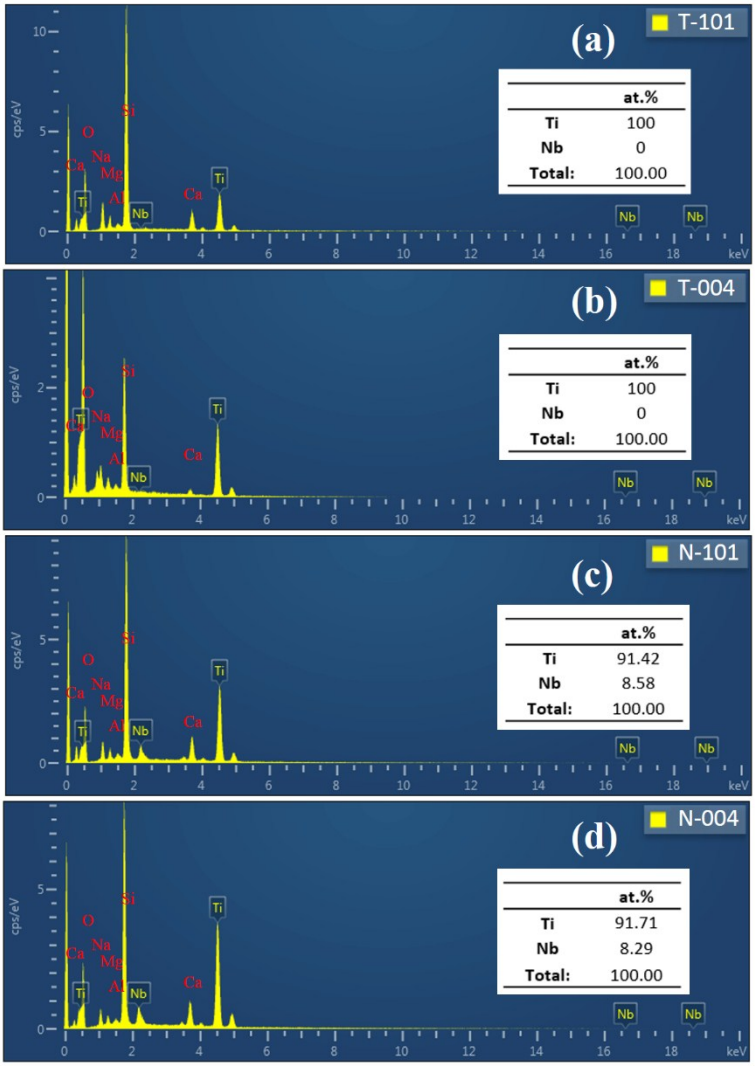

Fig. S2 EDS data of TiO_2-RO (a), TiO_2-004 (b), NTO-RO (c) and NTO-004 (d) on the soda-lime glass. The chemical elements marked with red words show the EDS data of soda-lime glass.

3. XPS spectra of TiO_2 and NTO Thin Films

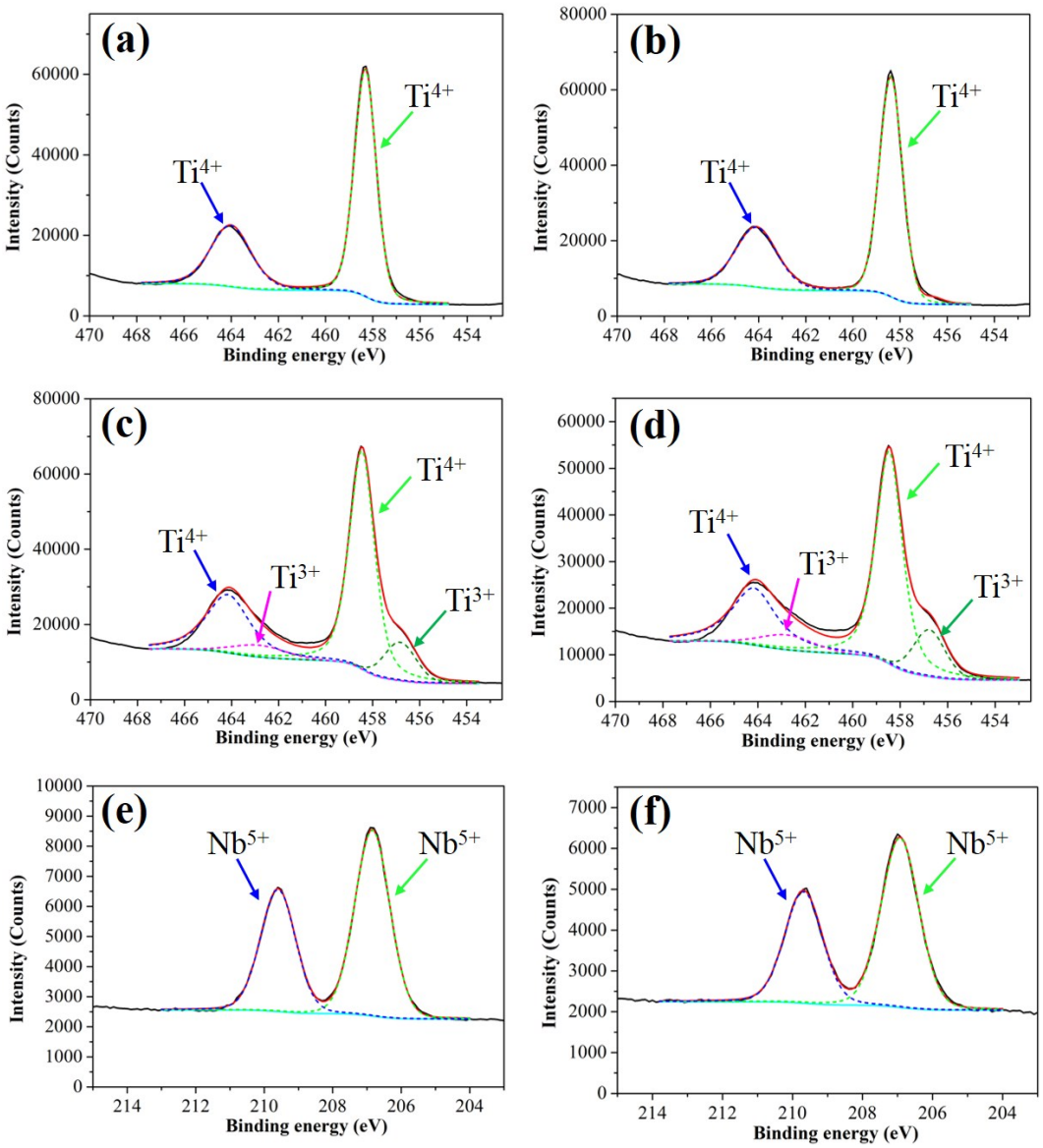

Fig. S3 XPS spectra of TiO_2-RO (a), TiO_2-004 (b), NTO-RO (c) and NTO-004 (d) thin films showing Ti^{4+} and Ti^{3+} state for the $2p_{3/2}$ transition. XPS spectra of NTO-RO (e) and NTO-004 (f) thin films showing Nb^{5+} state for the $3d_{5/2}$ transition. The data was treated with a Shirley background and individual Gaussian/Lorentzian functions for Ti^{4+}, Ti^{3+} and Nb^{5+} final states.

4. AFM height images of TiO_2 and NTO Thin Films

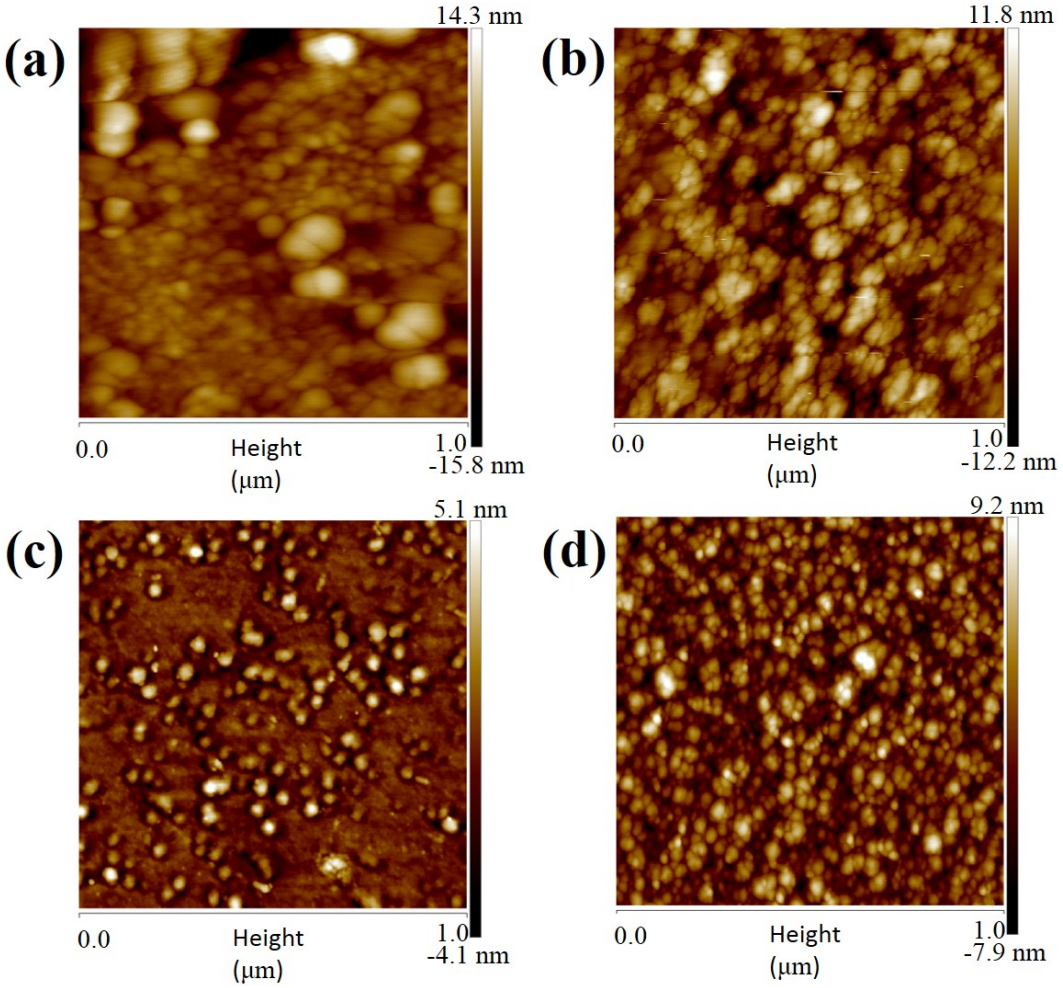

Fig. S4 AFM height images of TiO_2-RO (a), TiO_2-004 (b), NTO-RO (c) and NTO-004 (d) thin films.

5. Additional photocatalytic degradation figures

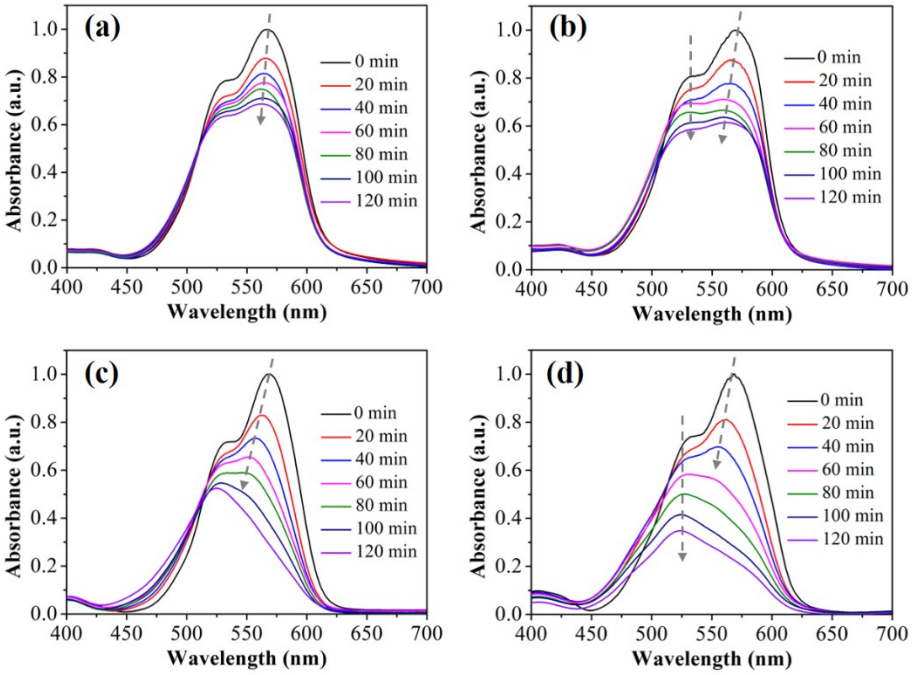

Fig. S5 Variation of the absorption spectra of a surface-coated Rh B degraded by TiO_2-RO (a), TiO_2-004 (b), NTO-RO (c) and NTO-004 (d) thin films under simulated solar light irradiation.

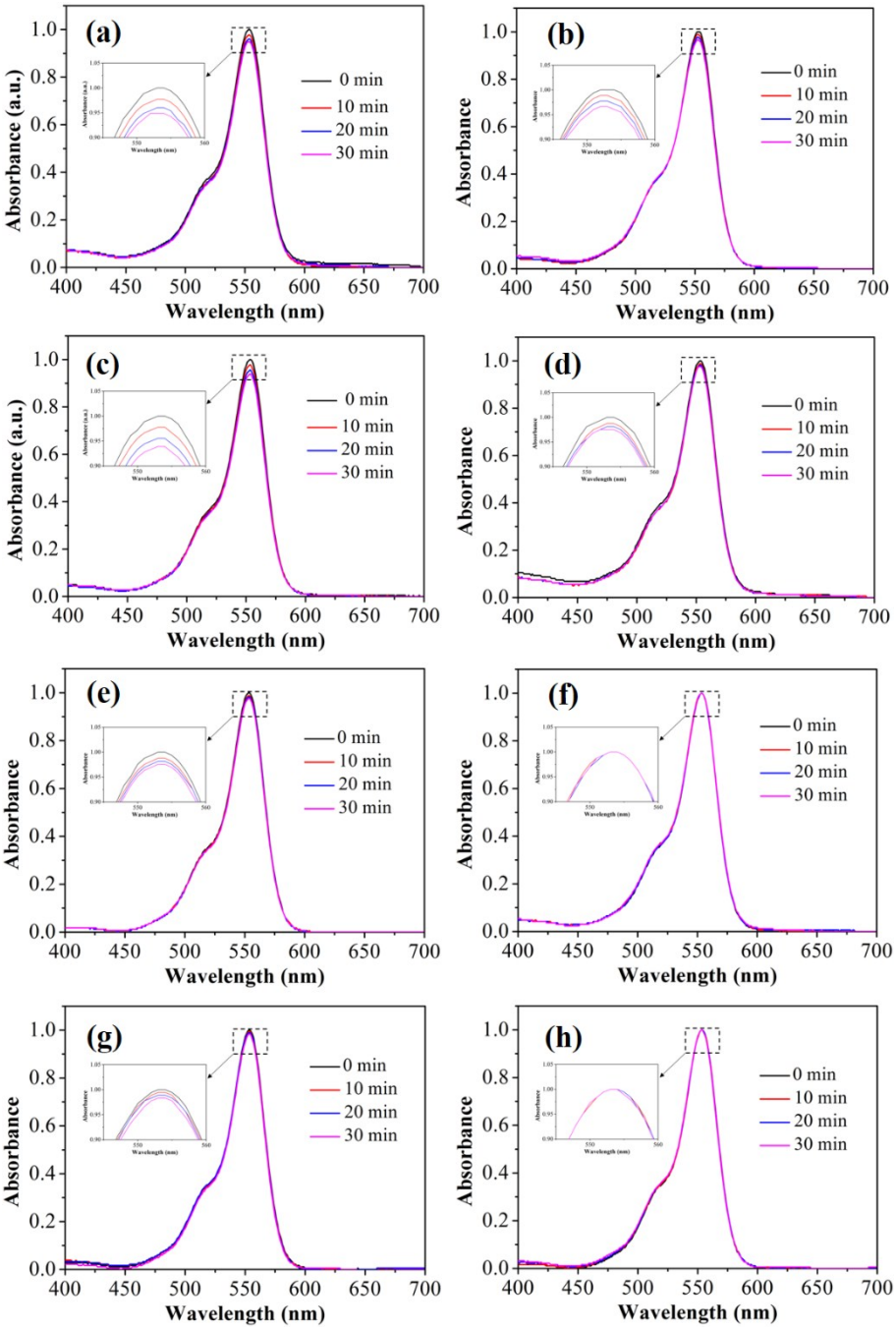

Fig. S6 Variation of the absorption spectra of RhB solution degraded by NTO-004 and TiO_2-004 thin films under single-wavelength LED irradiation. NTO-004: (a), (c), (e) and (g). TiO_2-004: (b), (d), (f) and (h). 365nm: (a) and (b). 515nm: (c) and (d). 650 nm: (e) and (f). 780 nm: (g) and (h).

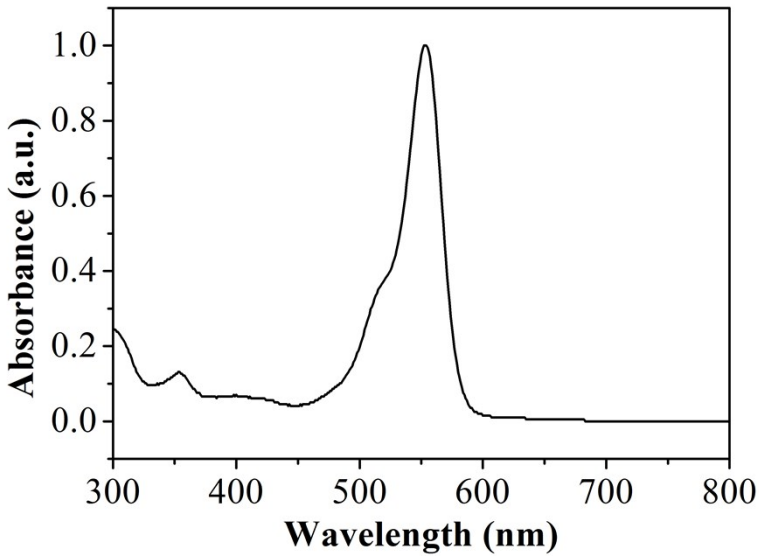

Fig. S7 The absorption spectra of Rh B solution.