## **Electronic supplementary information (SI):**

## **SI-Experimental procedures**

All substances used in this study were analytical grade and used without further purification. Deionized water was used in all experiments.

Synthesis of nc-TiO<sub>2</sub> films.<sup>14</sup> Anatase nanocrystalline titanium oxide (nc-TiO<sub>2</sub>) colloid as paste was purchased from the DyeSol company. Microscope glass slides (MGS) or conductive indium-tin-oxide (ITO)-coating glasses, used as the substrates for the nc-TiO<sub>2</sub> films, were cleaned by sonicating in acetone for 30 min and then in deionized water for another 30 min prior to use.  $Nc-TiO_2$  film was prepared by the doctor blade method using Scotch tape as the spacer. Following drying in air for 30 min, film was sintered at 723 K for 20 min. The resulting film was an average 4  $\mu$ m thick checked by a profilometer (Alpha-Step 200, Tencor Instruments). Subsequently, the film was put into a desired-concentration monometallic sodium orthophosphate solution for 1 h. After that, the film was rinsed with deionized water, dried naturally in air for 0.5 h, and then sintered at 723 K for 30 min. The un-modified and phosphate-modified nc-TiO<sub>2</sub> films are designated as TF and XP-TF, respectively, in which X indicates the concentration of sodium orthophosphate solution used. The film on MGS was cut into  $1.0 \times 1.5 \text{ cm}^2$  pieces and stored in a dry atmosphere for TAS measurements. The film on ITO glass was cut into  $1.0 \times 2.5 \text{ cm}^2$  pieces with TiO<sub>2</sub> surface area of  $1.0 \times 1.5$  cm<sup>2</sup>. To make a photoelectrode, an electrical contact was made with ITO substrate by using silver conducting paste connected to a copper wire which was then enclosed in a glass tube. The working geometric surface area of TiO<sub>2</sub> was  $1.0 \times 1.0$  cm<sup>2</sup>, where the remaining area was covered by epoxy resin.

*Characterization of nc-TiO*<sub>2</sub> *films*.<sup>14</sup> The film samples were characterized by X-ray Diffraction (XRD) with a Rigaku D/MAX-rA diffractometer (Japan), using CuK $\alpha$  radiation ( $\alpha$ = 0.15418 nm), and an accelerating voltage of 30 kV and emission current of 20 mA were employed. Scanning Electron Microscopy (SEM) observations were carried out on a Philips XL-30-ESEM-FEG operated at an accelerating voltage of 20 kV. The ultraviolet-visible (Uv-Vis) absorption spectra of film samples were recorded with a Model Shimadzu UV2550 spectrophotometer. The Fourier transform infrared spectra (FT-IR) of film samples were collected with a Bruker Equinox55 Spectrometer, using KBr as diluents. The surface composition and elemental chemical state of film samples were examined by X-ray Photoelectron Spectroscopy (XPS) using a Kratos--AXIS

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ULTRA DLD apparatus with Al(Mono) X-ray source, and the binding energies were calibrated with respect to the signal for adventitious carbon (binding energy = 284.6 eV).

Transient absorption spectra (TAS) of charge carriers of nc-TiO<sub>2</sub> films were measured by the laser system corresponding to the microsecond-millisecond ( $\mu$ s-ms) timescale described previously,<sup>20</sup> in which a PTI GL-3300 nitrogen laser was used as the excitation source (337 nm, 0.4 mJ/pulse, 2 Hz, and 1 ns pulse duration) and a 100 W tungsten lamp provided the probe light. A liquid light guide was utilized to transmit the laser pulse to the film sample. For controlling the intensity of used laser, optical neutral filters were placed between the light guide and the sample. The wavelength of probe light was controlled by monochromators before and after the film sample. The photocurrent from the detectors was processed by an AC-coupled preamplifier to extract the transient signal, which was magnified by a home-built amplifier-filter system. The signal was recorded with a digital oscilloscope (Tektronix TDS220) and transferred to a computer for analysis. The DC offset of the photocurrent from the detector was subtracted using the preamplifier, and thus small absorbance change ( $<10^{-5}$ ) could be measured. The film samples were placed in a sealed quartz cuvette for TAS measurements. For the films, the transient absorption studies were carried out under different atmospheres (or water systems). All TAS signals were obtained following averaging of 100-300 pulses. In this work, ∆OD means the transient absorption change.

**Temperature-programmed desorption (TPD)** of oxygen was conducted in a flow apparatus built by ourselves.<sup>15</sup> Sample powder (30 mg) was pretreated in a Pyrex tube (i.d. 6 mm) at 275 °C for 30 min by an ultra-high-pure He flow. After the treatment, the temperature was cooled to 25 °C. For  $O_2$  adsorption saturation, the sample was continuously blown with ultra-high-pure  $O_2$  for 90 min at 25 °C. After  $O_2$  adsorption, the sample was flushed in ultra-high-purity He flow for removal of physically adsorbed  $O_2$  on the oxides. An  $O_2$ -TPD profile of the sample was recorded by increasing the temperature from 25 to 700 °C at a heating rate of 10 °C/min under 20 mL/min of ultra-high-purity He flow. The desorbed  $O_2$  was analyzed by a gas chromatograph (GC-2014, SHIMADZU) with a TCD detector.

**Photoelectrochemical experiments** were performed in a glass cell using a 150 W Xenon light with a stabilized current power supply as the illumination source and 0.5 M NaClO<sub>4</sub> solution as electrolyte.<sup>14</sup> The working electrode was the nc-TiO<sub>2</sub> film (1.0 cm<sup>2</sup>) illuminated from the ITO

glass side. Platinum wire (99.9%) was used as the counter electrode, and a saturated KCl Ag/AgCl electrode was used as the reference electrode to which all the potentials in the work were referred at 25 °C. Oxygen-free nitrogen gas (or high-purity  $O_2$  gas) was used to bubble through the electrolyte before and during the experiments. Applied potentials were controlled by a commercial computer-controlled potentiostat (LK2006A made in China). For comparison, the I-V curves were also measured in the dark.

*Analysis of hydroxyl radical.*<sup>22</sup> A piece of nc-TiO<sub>2</sub> film ( $2.0 \times 3.6 \text{ cm}^2$ ) was fixed in  $2 \times 10^{-4}$  M coumarin aqueous solution in a quartz reactor of 50mL. Prior to irradiation, the reactor was purged with the desired gas under magnetically stirring for 0.5 h to ensure the establishment of an adsorption/desorption equilibrium. At given irradiation time, a certain amount of the solution is transferred into a Pyrex glass cell for the fluorescence measurement of 7-hydroxycoumarin at around 456 nm under the light excitation of 332 nm with a spectrofluorometer (Perkin Elmer LS55).

*Photocatalytic experiments*. The photocatalytic activity of nc-TiO<sub>2</sub> film was measured by degrading gas-phase aldehyde and liquid-phase phenol, respectively. For the photocatalytic degradation of gas-phase aldehyde, the nc-TiO<sub>2</sub> film fixed in a Pyrex glass cylindrical reactor with diameter of 7.0 cm and effective volume of 640 mL was illuminated by a 9 W ultraviolet lamp of 365 nm. A mixed gas containing a desired-content  $O_2$  and aldehyde was introduced to go through the reactor. Prior to irradiation, the gaseous mixture in the reactor was placed in dark for 20 min to reach adsorption-desorption equilibrium. The aldehyde concentration was measured with a gas chromatograph (GC-2014, SHIMADZU) equipped with a flame ionization detector.

**Liquid-phase photocatalytic experiments** were performed in a 50 mL photochemical glass reactor at room temperature at atmospheric pressure. A 150 W spherical xenon lamp which was positioned 10 cm away from the reactor was used as the light source to excite the photocatalytic reaction. In a typical photocatalytic experiment, an nc-TiO<sub>2</sub> film was fixed vertically in the 50 mL of 3 mg·L<sup>-1</sup> phenol solution. Prior to irradiation, the reactive system was magnetically stirred and bubbled with different gas (N<sub>2</sub> / air / O<sub>2</sub>) in the dark for 30 min to ensure anaerobic or aerobic conditions in the reaction system. The phenol concentration after photocatalytic reactions for 1 hour was measured by the 4-aminoantipyrine spectrophotometric method at the characteristic optical adsorption (510 nm) of phenol with a Shimadzu UV-2550 spectrophotometer.

**SI-figure 1** Temporal profiles of transient absorption spectra of un-modified (A) and phosphate-modified nc-TiO<sub>2</sub> films (B) in air.





**SI-figure 2** Curves of  $O_2$  temperature-programmed desorption on un-modified and phosphate-modified nc-TiO<sub>2</sub> powders obtained from the corresponding films by scraping.



SI-Figure 3 Amounts of formed hydroxyl radicals on un-modified and phosphate-modified  $nc-TiO_2$  films in N<sub>2</sub>-bubbled and air-saturated water after irradiating for a period of time.







**SI-Figure 4** I-V curves under illumination and in the dark of TF and phosphate-modified TF in the  $N_2$ - and  $O_2$ -purged systems. Potentials are measured against a Ag/AgCl (sat KCl) reference electrode in a 0.5 M NaClO<sub>4</sub> (aq) solution.



**SI-Figure 5** Photocatalytic degradation rates of gas-phase aldehyde (A) and liquid-phase phenol (B) on un-modified and phosphate-modified nc-TiO<sub>2</sub> films under different O<sub>2</sub>-content conditions (Initial concentration of aldehyde: 106 ppm, irradiation time: 1.5h; and initial concentration of phenol:  $3\text{mg}\cdot\text{L}^{-1}$ , irradiation time: 1h).

