Supplementary Information to

Enhanced Solar Absorption, Visible-Light Photocatalytic and Photoelectrochemical Properties of Aluminium-reduced $BaTiO_3$ nanoparticles

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Contents

1. Experimental details

Synthesis of the samples

A typical hydrothermal synthesis for $BaTiO_3$ nanocubes is given as following: all the reagents are of analytical grade and used without further purification. 15 mL $Ba(NO_3)_2$ (0.2 M) and 15 mL $Ti(SO_4)_2$ (0.2 M) were initially mixed together and then 20 g KOH is added directly into the mixture with constantly stirring. When the reaction mixture was cooled to room temperature in the air, it was then transferred into a 50 mL Teflon-lined stainless steel autoclave with 70% filling and heat treated at 180 °C for 12 h. After the autoclave was cooled and depressurized, the product was coolected and washed with deionized water and dried at 80℃ in air.

Preparation of Al-reduced $BaTiO_3$

The as-grown $BaTiO_3$ nanoparticles and Alumium were placed separately in a tube furnace and evacuated to a base pressure lower than 0.5 Pa. And then, Aluminum and $BaTiO_3$ samples were heated together at 600 ℃, 700 ℃ and 800 ℃ for 6 h, 12 h and 18 h, and then cooled to room temperature under vacuum condition. Finally, the color of $BaTiO_3$ nanoparticles turned from white to black.

Characterization

XRD patterns were obtained from a Rigaku D/Max-2000 diffractometer with Cu Kα radiation (λ = 1.5418 Å) at 40 kV, 100 mA at room temperature. Field emission scanning electron miscroscopy (FESEM) images were taken on a JSM-7800F microscope with energy-dispersive X-ray spectroscopy. Transmission electron microscope (TEM) was obtained by a JSM-2100F/HR microscope at an accelerating voltage of 1600V. The optical properties of the samples were analyzed using a UV-3100 Shimadzu ultraviolet-visible-infrared spectrophotometer equipped with an integrating sphere, in reflectance mode. Brunauer-Emmett-Teller (BET) surface area was measured by an ASAP-2020 Micromerities USA. X-ray photoelectron spectroscopy (XPS) was carried out on an Axis Ultra spectrometer. The binding energies were collected for Ti 2*p*, Ba 3*d*, and O 1*s* regions with the C1*s* reference of 284.5 eV.

Photocatalytic experiments

Photocatalytic activities of the $BaTiO_3$ samples were evaluated by the methylene blue and methyl orange decomposition under visible and solar-light irradiations with a 500 W Xenon lamp. In each experiment, 0.05 g of the photocatalysts was added into 100mL of 10 mg/L methylene blue or methyl orange solution, and stirred constantly in the dark for 30 min to ensure an adsorption/desorption equilibrium. The concentrations of the dyes were checked for each 30 min by using a MAPADA UV-3100PC UV-vis spectrophotometer.

Chemical oxygen demand measurements

The oxygen equivalent of the organic matter of a sample, i.e., chemical oxygen demand (COD), was measured by using a SPECTROQUANT NOVA 60 Photometer. The reagents for COD analysis and 3 mL of samples taken at different time intervals during photocatalytic reaction were mixed together in glass cells and digested in a Spectroquant TR 320 thermodigester for 2 h at 421 K. After digestion, the mixture was cooled to room temperature and the COD was measured using the photometer. The COD was measured for the original solution and the centrifuged sample taken out at different time intervals.

Photoelectrochemical cell (PEC)

To characterize the photoelectrochemial performance of the samples, a typical three-electrode system was utilized to conduct electrochemical measurements with an electrochemical workstations (CHI750E, CH Instruments), in which the BTO film or BTO-800 film are prepared on ITO substrate by dip-coating method, a Pt wire, and an Ag/AgCl electrodes were used as the working counter, and reference electrode. 1.0 M NaOH aqueous solution was used as the supporting electrolyte to maintain the stability of films. A solar simulator (AM 1.5) with a power of 100 mW/cm^2 was used as the illumination source. Photocurrent ON/OFF cycles were measured using the same electrochemical workstation coupled with a mechanical chopper. The solar-to-hydrogen (STH) efficiencies (η) of photoanodes were calculated using the equation: □□

$$\eta = I\,(1.23 - V)\,/J_{\text{light}},$$

where V is the applied bias vs RHE, I is the photocurrent density at the measured bias, and *Jlight* is the irradiance intensity of 100 mW/cm^2 (AM 1.5G).

2. Schematic illustration

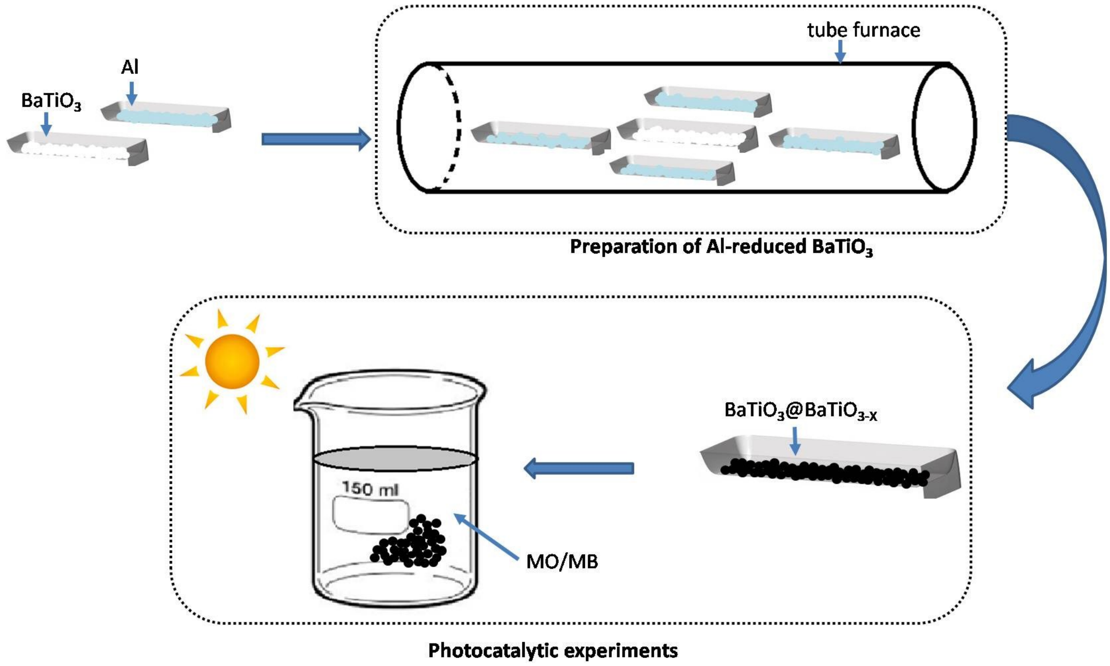

Figure S1. Schematic illustration of the Al-reduced course and solar light driven photocatalysis.

3. EDS results

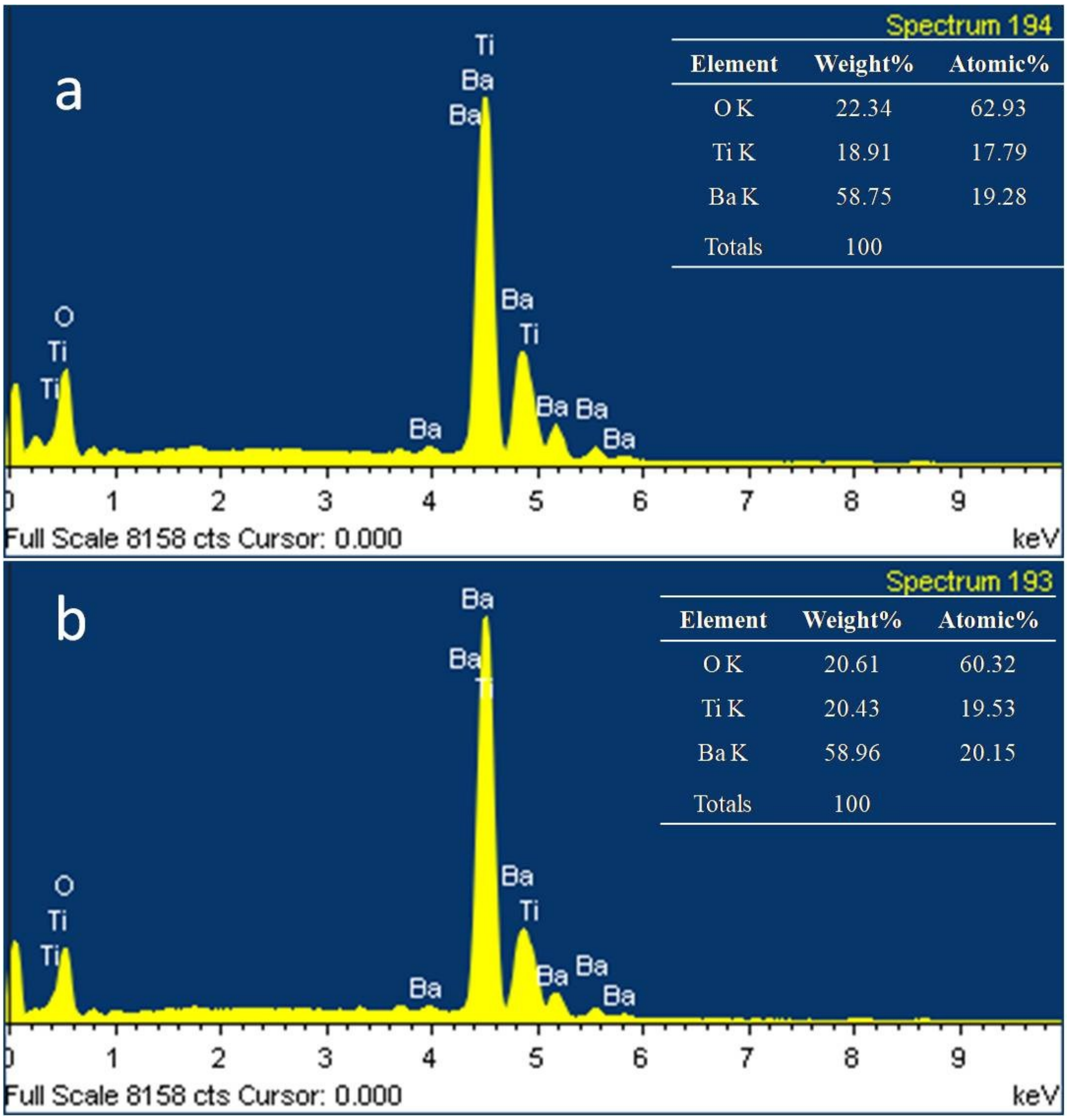

Figure S2. EDS results of pristine $BaTiO_3$ (a) and Al-reduced $BaTiO_3$ at 800 ^{o}C (b).

4. Heat treatment without Al

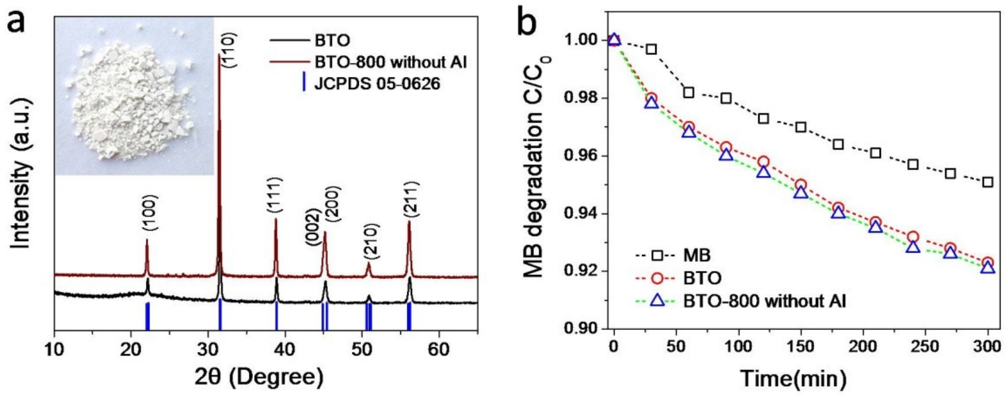

Figure S3. The XRD (a), optical photograph (inset of a) and visible-light driven MB photodegradation (b) of $BaTiO_3$ heated at 800 ^oC under vacuum condition without Al.

5. XPS spectra

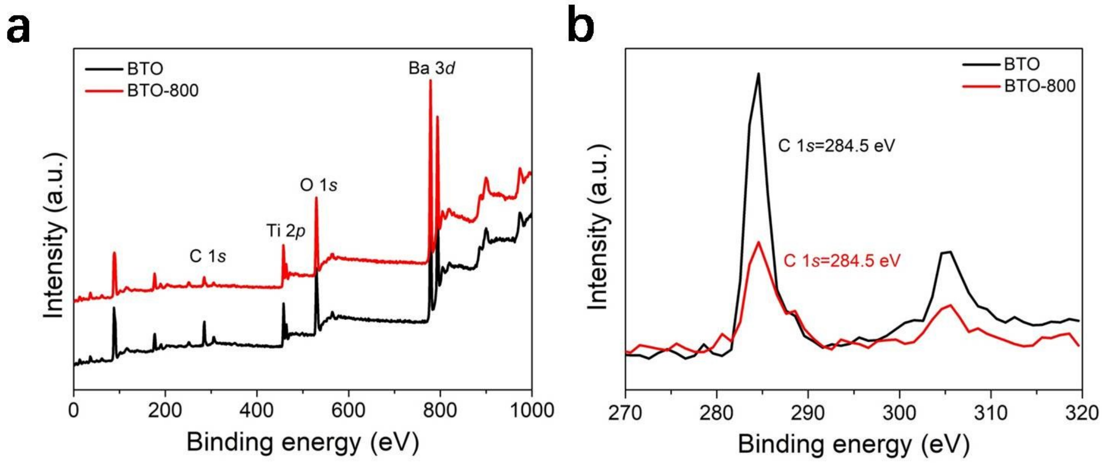

Figure S4. XPS survey spectra (a) and C 1*s* reference (b) of the obtained $BaTiO_3$ and Al-reduced $BaTiO_3$ at 800 ^{o}C.

6. Optical photographs

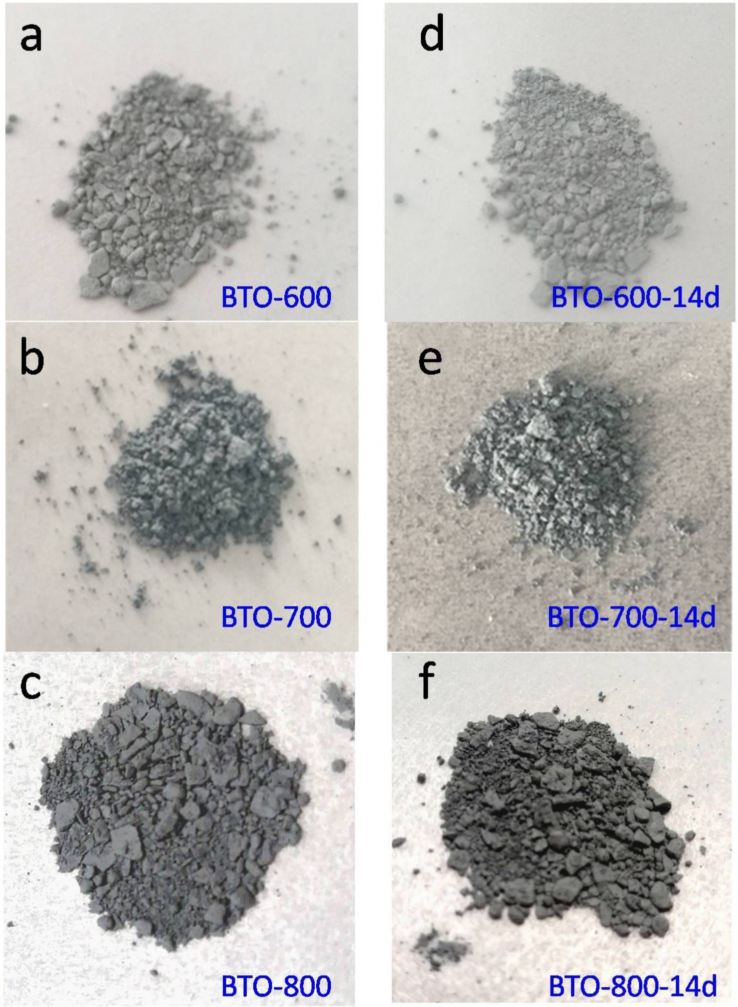

Figure S5. The optical photographs of BTO-600, BTO-700 and BTO-800 after five cycling tests (a,b,c) and exposing to air for two weeks (d,e,f).

7. Photocatalytic decomposition

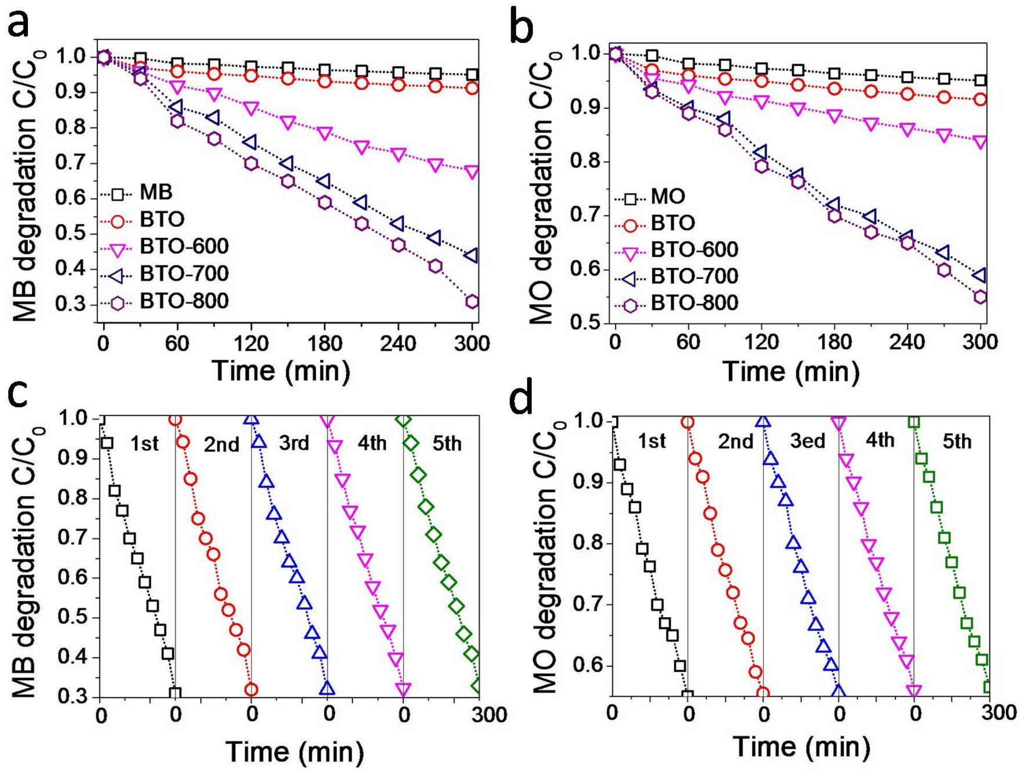

Figure S6. (a) Photocatalytic decomposition of methylene blue (MB) and (b) methyl orange (MO) with the pristine $BaTiO_3$ and Al-reduced $BaTiO_3$ under solar-light irradiation. Cycling tests of solar-light driven photocatalytic activity of BTO-800 for MB (c) and MO (d) photodegradations.

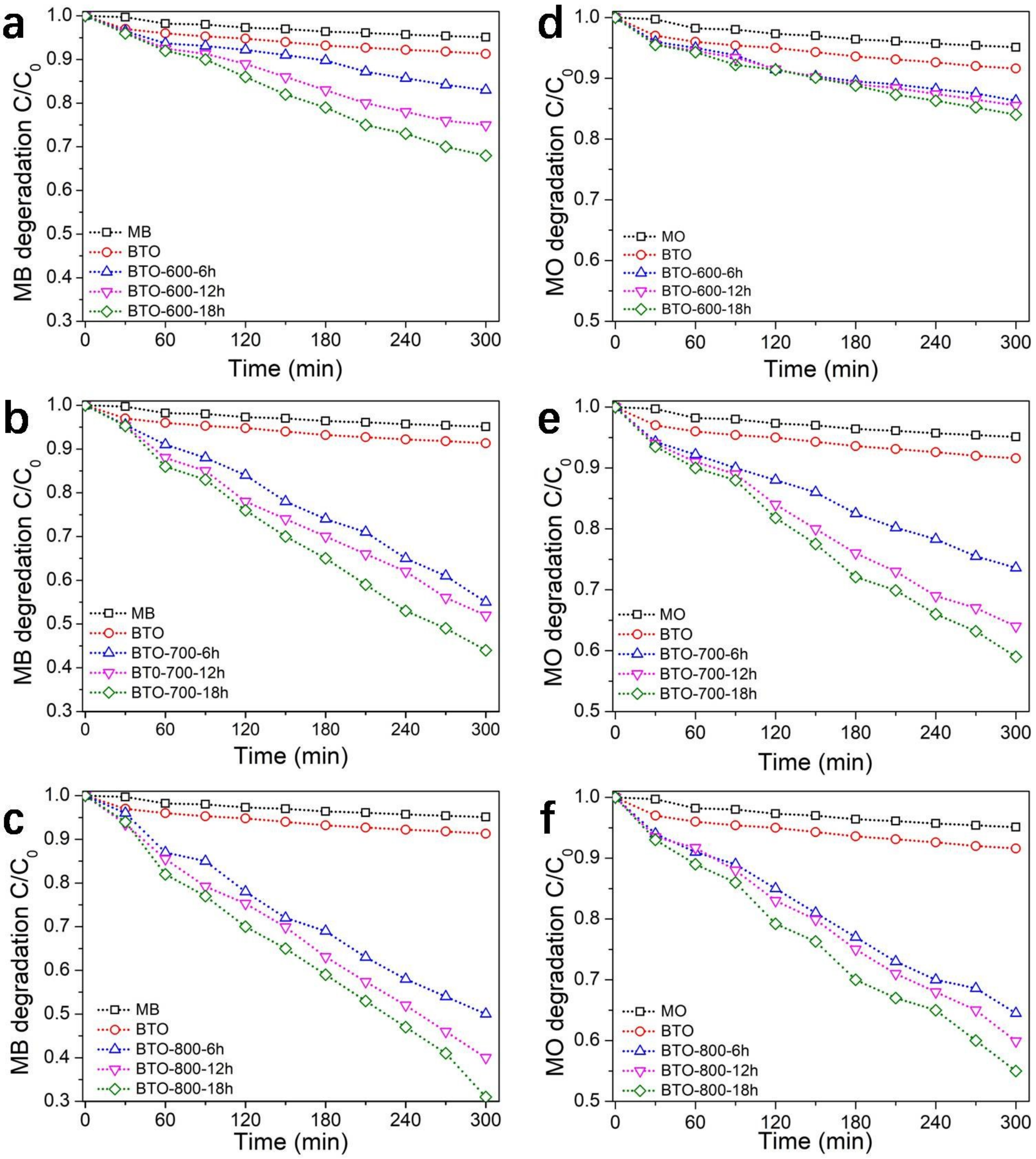

Figure S7. Photocatalytic activity of black $BaTiO_3$ at different Al reduction time (6 h, 12 h and 18 h) and temperature (600 ^oC, 700 ^oC and 800 ^oC): (a, b, c) for the degradation of MB; (d, e, f) for the degradation of MO.

8. Temporal evolutions of the absorption spectra

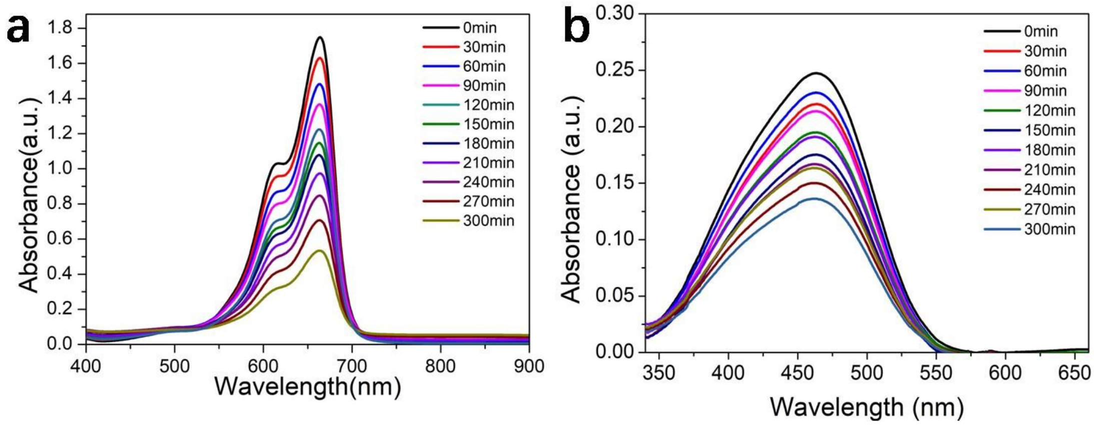

Figure S8. The temporal evolutions of all the absorption spectra of the MB (a) and MO (b) solution (10^{-5} mol/L) degraded by BTO-800 under Xe lamp light irradiation.

9. Air stability

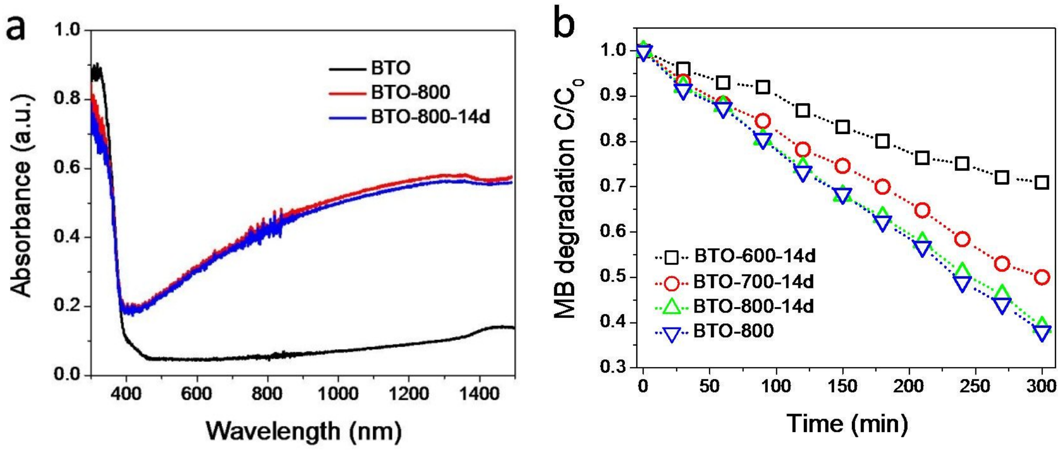

Figure S9. UV-vis spectra (a) and photocatalytic activity (b) of Al-reduced $BaTiO_3$ after exposing to air for two weeks.

10. COD results

Table S1. The COD values of MB and MO solutions with respect to visible irradiation time by using BTO-800 catalyst

COD / Dyes	COD value (mg/L) at different irradiation time (min)										
	0	30	60	90	120	150	180	210	240	270	300
MB	9.9	8.1	7.3	7.1	6.9	6.4	6.1	5.8	6.7	5.3	4.8
MO	13.5	11.0	10.8	10.7	10.4	10.3	10	9.9	9.5	9.3	9.0