Electronic Supporting Information (ESI) For
Microcrystalline sodium tungsten bronze nanowire bundles
as efficient visible light-responsive photocatalysts

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Experimental Details:

Materials Preparation. Na2WO4·2H2O (3.30 g, 0.01 mol), NaCl (5.85 g, 0.1 mol) and 70 mL of distilled water were introduced into a 100-mL beaker under constant stirring at room temperature to give a stable and clear solution. Then, the pH value of the mixed solution was adjusted to 2.0 by adding dilute hydrochloric acid solution. After stirring for 30 min, the mixture solution was transferred into a Teflon-lined autoclave of 100 ml capacity. The autoclave was heated to 180°C with the heating rate of 2°C min⁻¹ and maintained at 180°C for different times and then cooled to room temperature naturally. The resulting solid product was filtered and washed repeatedly with distilled water and then dried at 80°C for 4 h. To get h-WO3 products, the Na-HT precursors were immersed in 1M HNO3 solution for 24 h. Then the mixture solution was transferred into a Teflon-lined autoclave and maintained at 180°C for 24 h. Last, the products were filtered, washed with distilled water, and dried in air.

Characterization. The crystal structure of the samples were determined by Powder X-ray diffraction (XRD) patterns (Bruker D8, Germany), using Cu Kα radiation (λ =1.54178 Å) at a scanning rate of 0.02°S⁻¹ in the 2θ range from 10° to 70°. The
operation voltage and current were maintained at 40 kV and 40 mA, respectively. The chemical composition was analyzed by a Genesis 2000 energy-dispersive X-ray spectrometer (EDX) with SUTW-Sapphire Detector at 20 kV. The morphology of the samples was observed by Scanning electron microscopy (JSM-7600F, 10 kV) and Transmission electron microscopy (JEM-100CXII, 100 kV). High-resolution transmission electron microscopy (HRTEM) analyses were conducted with the use of JEOL model JEM 2010 EX instrument at the accelerating voltage of 200 kV. The powders were supported on a carbon film coated on a 3 mm diameter fine-mesh copper grid. A suspension in ethanol was sonicated, and a drop was dripped on the support film. The UV-visible diffuse reflectance spectrum of the sample was measured with a Shimadzu UV-2500PC double-beam spectrometer equipped with an integrating sphere attachment, and BaSO$_4$ was used as the reference material. The data were transformed into absorbance with the Kubelka-Munk function.

**Adsorption Test and Photocatalytic Activity Test. Adsorption test:** 30 ml of methylene blue solution (50 mg/L) was added to 30 mg of sample in a 50 mL Pyrex-glass cell in the dark. The suspension was stirred on a magnetic stirrer at a uniform speed of 300 rpm in a constant temperature bath. After 1 h adsorption time, through centrifugal separation and the concentration of methylene blue in the aqueous phase was determined using a Shimadzu UV-Vis spectrophotometer.

**Photocatalytic activity test:** 30 mg of the powdered samples were suspended in 30 mL of MB (50 mg/L for Na-HT, 10 mg/L for WO$_3$) at room temperature under air condition. The samples were kept with agitation in dark for 60 minutes to allow the adsorption equilibrium, the reactors were then irradiated with visible light emitted by a 500 W Xe arc lamp with a UV cutoff filter (λ>420 nm), At given irradiation time intervals, 3 mL aliquots were centrifuged to remove the catalyst. The absorption spectrum of the filtrate was measured on a UV-Visible spectrometer. To test its photocatalytic lifetime, the as-prepared Na-HT-48h was recycled and reused five times in the decomposition of MB under the same conditions. After each photocatalytic reaction, the aqueous solution was centrifuged to recycle the Na-HT-48h powders that were then dried at 80°C for another test.
**Theoretical Method.** Density-functional theory (DFT) calculations\(^1\) were carried out with a periodic supercell model with a plane-wave basis set implemented in the Cambridge Sequential Total Energy Package (CASTEP) code.\(^2\) Ultrasoft pseudopotential\(^3\) had been used to treat core electrons. The energy cutoff was set to 370 eV for the plane wave basis and the exchange-correlation functional is treated by PW91 form generalized gradient approximation (GGA-PW91).\(^4\) According the result of XRD in the experiment, the hexagonal WO\(_3\) with space group P6\(^3\)/m$$m$$m was used in this calculation. To achieve the accurate density of the electronic states, the k space integrations were done with the Monkhorst-Pack grids\(^5\) and k-point separation quality was set as 0.04 /Å corresponding to 4×4×8 k-point for the pure phase. Before the single point energy calculation, geometry optimization was done, and the self-consistent convergence accuracy was set at 1×10\(^{-5}\) eV/atom, the convergence criterion for the force between atoms was 2×10\(^{-2}\) eV/Å, the maximum displacement was 1×10\(^{-3}\) Å.

The 2×2×2 WO\(_3\) crystal cell was selected to construct doped configuration, corresponding to 96 atoms supercell. For the natrium doping model, the Na atom was introduced at interstitial sit in the supercell crystal, and the geometry optimization of doping supercell was carried at Γ point. Also with the k-point separation quality of 0.04 /Å, 2×2×3 k-point for the optimized Na doped configuration was used for the electronic properties calculations.

**Reference**


**Fig. S1** A) XRD patterns of h-WO$_3$ (a) and Na-HT samples prepared by hydrothermal method at 180°C for different reaction times: (b) 6h, (c) 12h, (d) 24h, (e) 48h; B) Diffraction peak positions of the (001) plane in the range of 2θ = 22.6°-23.2°.
**Fig. S2** TEM and SEM images of the as-prepared samples with reaction times of (a) 6h, (b) 12h, (c) 24h, (d) 48h.

**Fig. S3** Respective EDS spectra of h-WO$_3$ (a) and different and Na-HT samples prepared for different reaction times b) 6 h, c) 12 h, d) 24 h, e) 48 h.
**Fig. S4** The lifetime for photodegradation of MB on Na-HT-48h sample.

**Fig. S5** Bar plot showing the remaining methylene blue in solution: (a) C-WO₃, (b) h-WO₃, and Na-HT samples prepared for different reaction times c) 6h, d) 12h, e) 24h, f) 48h in the dark after 60 min stirring.
**Fig. S6** UV-Vis absorption spectra of different samples: a) Na-HT-6h, b) Na-HT-12h, c) Na-HT-24h, d) Na-HT-48h, e) h-WO₃, f) Na₂WO₄; inset is the calculation diagram of their band gaps.

**Fig. S7** DOS and PDOS plots calculated for undoped h-WO₃ and Na⁺-doped WO₃: (a) pure h-WO₃ model, (b) Na⁺-doped WO₃. The zero energy is set at the valence band maximum of the pure phase the dotted line represents the Fermi level.