Experimental Section

Synthesis of WO_x Nanostructures.

All chemicals were analytical grade and commercially available and used as received without further purification. In a typical sample preparation procedure, 0.01 mol ammonium paratungstate, 0.24 mol ammonium nitrate and different amounts of glycine (0 mol, 0.05mol, 0.1 mol, 0.2mol) were dissolved into 150 mL deionized water, and then stirred to obtain a homogeneous solution. The mixture was filled into a 400 mL glass, and was heated in air on a controllable muffle.

Characterization of the products.

X-ray diffraction study of the powders were carried out in an X-ray diffraction study of the powders were carried out in an X-ray diffractometer using Cu K α radiation (X-ray diffraction (XRD); Rigaku, D/max-RB12), and the 20 angle was varied from 10° to 90° in 0.02° increments. An STA-449F3 (NETZSCH-Gerätebau GmbH, Germany) with a mass spectrometer (QMS403C) was used to conduct thermogravimetric analysis (TG), differential scanning calorimetry (DSC) and gas-phase analysis of gels obtained by quenching before being ignited at a heating rate of 5 K/min in argon atmosphere. The morphology and particle size of powders were observed by field emission scanning electron microscopy (FESEM, ZEISS ULTRA 55 Field-Emission Scanning Electron Microscope) and a Tecnai G² F20 transmission electron microscopy (TEM) operated at an acceleration voltage of 200kV. Energy-dispersive X-ray (EDX) analysis was obtained with an EDAX detector installed on the same high resolution transmission electron microscopy (XPS) was

performed with the PHI-5300 spectrometer.

Photocatalytic Test.

The photocatalytic activities of $W_{18}O_{49}$ powders were evaluated by degradation of MB in an aqueous solution. The photocatalyst (1 g•L-1) was added to an aqueous solution of MB (100 mL; 40 mg•L-1) in a quartz vessel at room temperature in air. And then 2.0 mL of a 30% hydrogen peroxide (H_2O_2) solution were added as electron acceptor. To minimize the heat effect, the sample was placed about 5 cm away from the lamp. The suspension was first sonicated for 1 min. Before light was turned on, the solution was stirred continuously for 30 min in the dark to establish an adsorption-desorption equilibrium. Then, this suspension was radiated with simulated sunlight (Xenic lamp as light source, 350 W, wavelength from 200 to 800 nm). After each given irradiation time, 1 mL of the mixture was withdrawn and separated by centrifuging to remove any suspended solids. The degradation process was monitored by a UV-vis spectrophotometer (UV-3600, Shimadzu, measuring the maximum absorption of MB at 664 nm). To study the self-degradations of MB solution, the same size carbon paper without WO₃ nanostructures was added into the MB solution under the same irradiation conditions, as show in Fig. S2

Theory explanation for the different conditions of the solution combustion synthesis.

The stoichiometric equilibrium combustion reaction (e.g., by using glycine as a fuel) can be described by the following scheme:

$$(NH_4)_6H_2W_{12}O_{40}+24NH_4NO_3+\frac{10}{3}\Phi C_2H_5O_2N+\frac{15}{2}(\Phi-1)$$
 O₂

$$\rightarrow 12WO_{3} + \frac{45 + 5\Phi}{3} N_{2} + \frac{20}{3} \Phi \text{Error!} \text{Error!} \text{CO}_{2} + \frac{183 + 25\Phi}{3} H_{2}\text{O};$$

 $\Phi < 1$ implies fuel-lean condition;

 Φ =1 means that the initial mixture does not require atmospheric oxygen for complete oxidation of the fuel;

 Φ >1 implies fuel-rich condition;

Supporting Figures



Figure S1 EDS spectrum of the as-prepared $W_{18}O_{49}$.



Figure S2 Results of TG–DSC analysis for the reaction with 0 mol glycine.



Figure S3 Changes of time-dependent UV-Vis absorbance spectra in the absent of

 $W_{18}O_{49}$ under visible-light irradiation for different times.