

Electronic Supplementary Information

Experimental

Photocatalyst preparation and characterization

Photocatalyst $W_2Fe_4Ta_2O_{17}$ was prepared by the conventional solid state route. In a typical procedure, the different oxide precursors, WO_3 , Fe_2O_3 and Ta_2O_5 of appropriate quantities conforming to the stoichiometric elemental ratio of $W : Fe : Ta = 1 : 2 : 1$ respectively, were mixed and ground thoroughly in a mortar until a physically homogeneous mixture was obtained. Then the sample placed in a pure alumina crucible was sintered in programmed furnace at 1000 °C for 10 h in static air atmosphere. After cooling to room temperature, it was again ground thoroughly and sintered under the same condition. This process was repeated for a third time also. A triple sintering was, thus, performed, which ensured the formation of crystalline chemically homogeneous photocatalyst sample.

Powder X-ray diffractograms of the photocatalyst sample was recorded with a Rigaku – D/MaX-2200V XRD instrument with $CuK\alpha$ (40 kV / 40mA) radiation ($\lambda = 1.5405 \text{ \AA}$) using graphite monochromator and Ni filter. Field emission scanning electron microscope (FESEM) pictures of the sample were obtained from JEOL – JSM 6700F instrument. Diffuse absorbance spectrum was recorded with Shimadzu UV – 2450 UV-Vis spectrophotometer. Inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Jobin-Yvon Ultima-C) instrumental technique was used in determining the elemental composition of the

photocatalyst sample.

Electron mediator and other chemicals

Organometallic complex M (electron mediator) was synthesized as described in previous work¹. All other chemicals and reagents were of highest purity commercially available and were used as such.

(1) Hollmann, F.; Witholt, B.; Schmid, A. *J. Mol. Catal. B Enzym.* **2003**, 19-20, 167.

Photobiosynthesis and Evaluation Techniques

Both photoregeneration of NADH and photoenzymatic synthesis of glutamate were carried out at room temperature (~ 20 °C) using a quartz cuvette reactor (3 mL). Reactions were carried out with 450 W Halogen lamp ($\lambda \geq 420$ nm) under Ar atmosphere. For the photoregeneration of NADH, 5 mg of $W_2Fe_4Ta_2O_{17}$ was stirred with 0.2 mM $[Cp^*Rh(bpy)H_2O]^{2+}$, 0.1 mM NAD and 5/20 mM EDTA based on 100 mM phosphate buffer (pH = 7.0). Concentration of NADH was spectrophotometrically measured at 340 nm (Biospec-mini, Shimadzu).

The photobiosynthesis of glutamate was carried out using the same composition as in NADH but with additional enzymatic reaction components of 5 mM $(NH_4)_2SO_4$, 0.1mM α -ketoglutarate and 20 U glutamate dehydrogenase. The concentration of photoenzymatically synthesized glutamate was analyzed by the colorimetry of quinoneimine dye at 490 nm using microplate reader². Samples from the reaction medium were incubated with glutamate oxidase

(0.2125 U/mL) / horseradich peroxidase (37.5 U/mL) system, including 1 mM 4-aminoantipyrine and 4 mM p-hydroxybenzene sulfonate as dye components.

(2) C. B. Park and D. S. Clark, *Biotechnol. Bioeng.* **2002**, 78, 229.

Table S1 Elemental composition (wt %) of the photocatalyst $W_2Fe_4Ta_2O_{17}$

	Element (wt %)		
	W	Fe	Ta
Measured*	31.3	18.6	30.7
Initially fixed	29.8	18.1	29.3

* By ICP-AES instrumental method

Observed stoichiometry (elemental ratio) W : Fe : Ta = 2.0 : 3.92 : 1.99

Initial stoichiometry (elemental ratio) W : Fe : Ta = 2.0 : 4.0 : 2.0

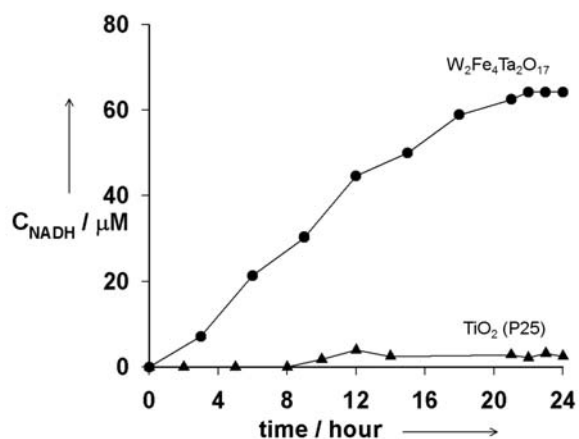


Figure S1 NADH photoregeneration time profiles under visible light irradiation for $\text{W}_2\text{Fe}_4\text{Ta}_2\text{O}_{17}$ and TiO_2 , respectively

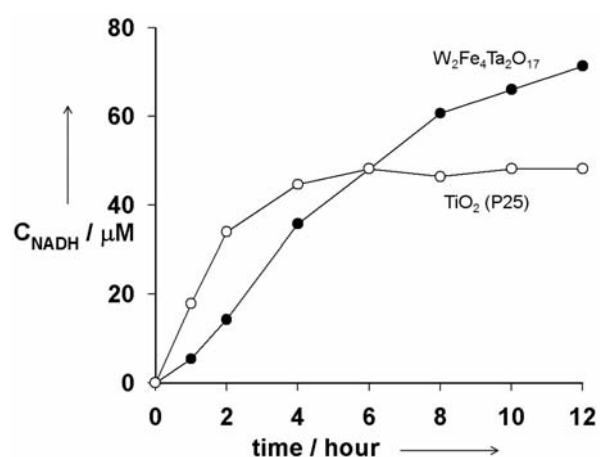


Figure S2 NADH photoregeneration time profiles under uv-visible light irradiation for $\text{W}_2\text{Fe}_4\text{Ta}_2\text{O}_{17}$ and TiO_2 , respectively

Photocatalyst $\text{TiO}_{2-x}\text{N}_x$ preparation

The visible light photocatalyst $\text{TiO}_{2-x}\text{N}_x$ ($x=0.01$) was prepared by the same process of the reference.³

(3) S. In, A. Orlov, F. Garcia, M. Tikhov, D. S. Wright and R. M. Lambert, *Chem. Commun.*, 2006, 4236 – 4238.