Supporting Information

Integration of Functionalized Two-Dimensional TaS$_2$ Nanosheets and

Electron Mediator for More Efficient Biocatalyzed Artificial

Photosynthesis

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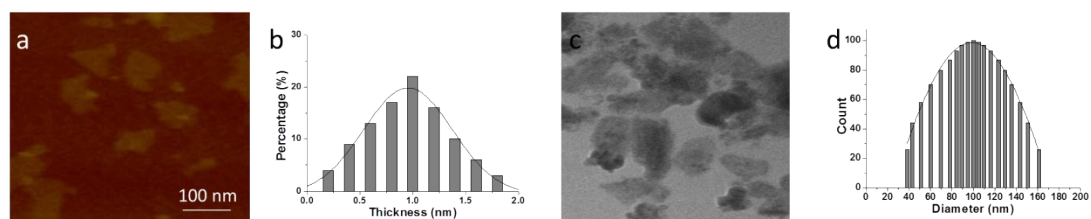
Figure S1. Characterization of as-made TaS$_2$ nanosheets dispersed in NMP. (a) AFM image, (b) thickness, (c) TEM image, and (d) size distribution.
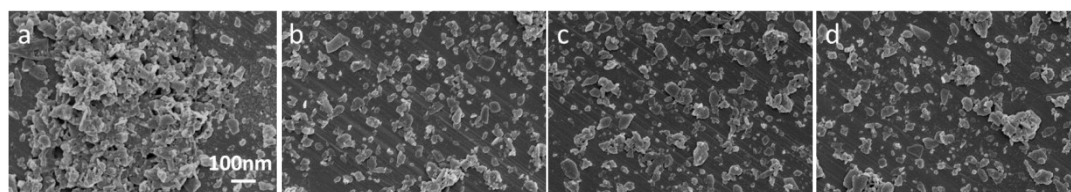

Figure S2. Scanning electronic microscope (SEM) images of (a) TaS$_2$, (b) TaS$_2$-PEG, (c) TaS$_2$-PEG-GR and (d) TaS$_2$-PEG-GR-M.
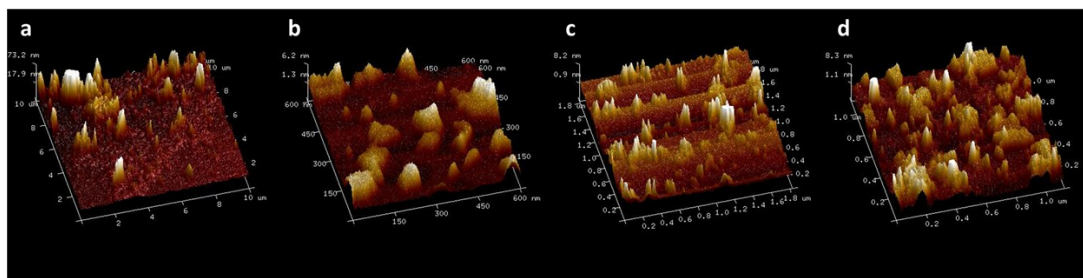
Figure S3. Atomic-force microscopy (AFM) 3D images of (a) TaS_2, (b) TaS_2-PEG, (c) TaS_2-PEG-GR and (d) TaS_2-PEG-GR-M.
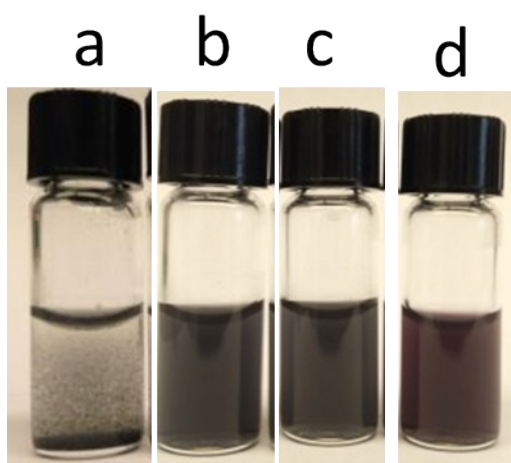

Figure S4. Photo images of (a) TaS_2, (b) TaS_2-PEG, (c) TaS_2-PEG-GR and (d) TaS_2-PEG-GR-M after storing in room temperature for one week.
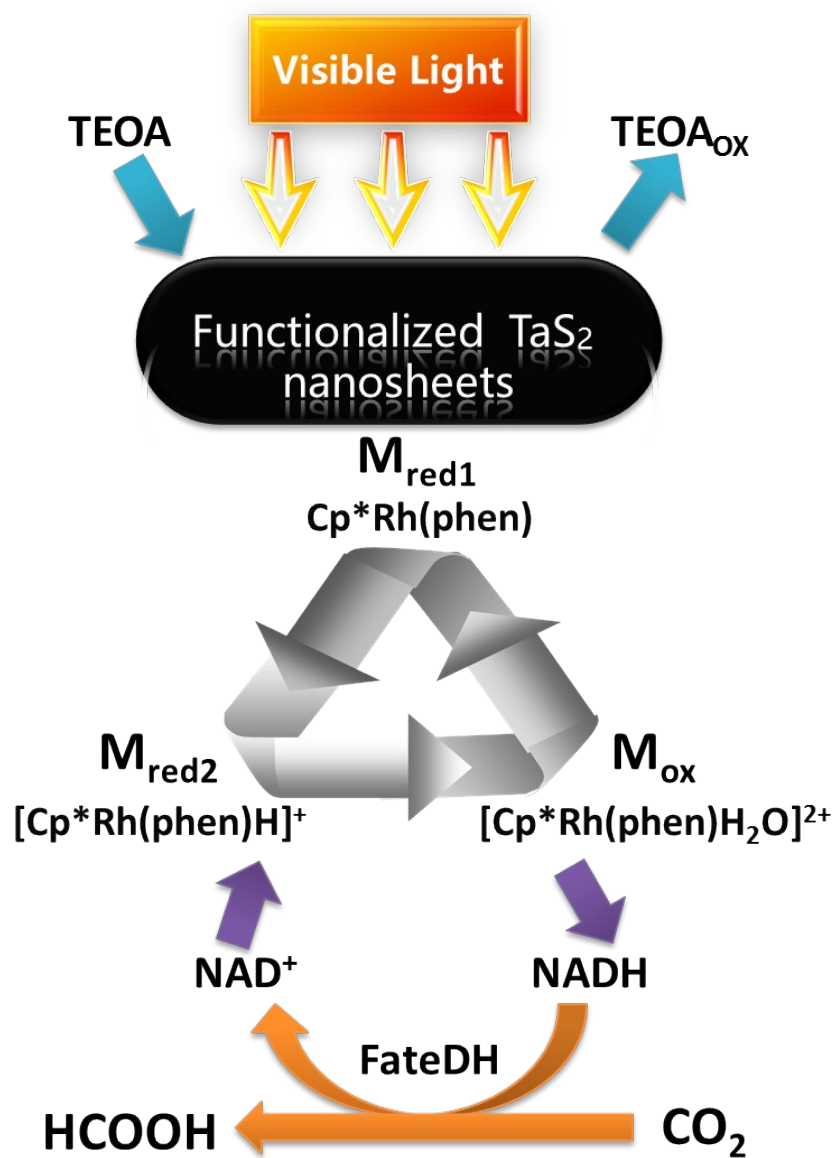
Figure S5. Schematic illustration of functionalized TaS_2 nanosheets-sensitized photo-regeneration of NADH

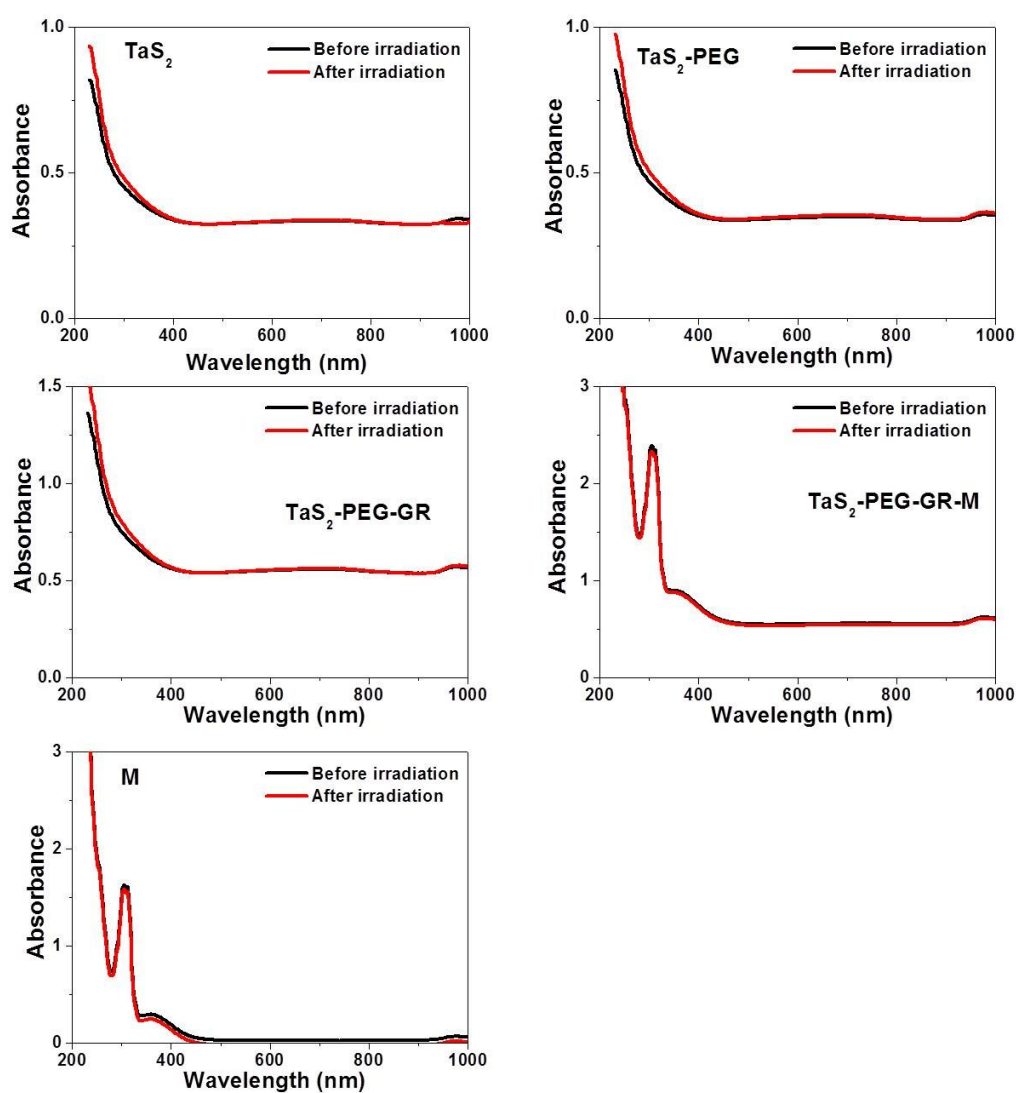**Figure S6.** UV-vis-NIR absorbance spectra of TaS$_2$ nanosheets and its functionalized derivatives, as well as the electron mediator M before and after being exposed to 5 h's irradiation of 450 W Xenon lamp with a 420 nm cut-off-filter. In all cases, the concentrations of TaS$_2$ and M were adjusted to the same level as used in the photo-enzymatic experiments, at 0.3 mg/mL and 0.25 mM, respectively.

Table S1. Element content of TaS_2-PEG-GR-M analyzed from EDS mapping

Element	Weight%	Atomic %
C	29.76	64.46
O	10.2	16.57
S	14.67	11.92
Ta	40.48	5.81
Rh	4.9	1.24
Total	100	100

Table S2. The yields of NADH regenerated from NAD^+ after 120 mins' irradiation by applying different concentration of TaS_2 nanosheets

Concentration of TaS_2 (mg/mL)	Yield of NADH (%)
0.1	20.2±3.0
0.2	30.2±1.7
0.3	39.7±1.9
0.4	42.5±2.0

Table S3. The yield of regenerated NADH and synthesized formic acid concentration by using different functionalized TaS_2 nanosheets

Photocatalyst	Electron mediator	Yield of NADH (%)	Concentration of formic acid (mM)
TaS_2	Free M	39.7±1.9	40.7±2.4
TaS_2-PEG	Free M	54.6±1.8	64.9±3.2
TaS_2-PEG-GR	Free M	64.2±2.9	74.4±2.6
TaS_2-PEG-GR-M	(Integrated)	83.9±2.2	101.4±3.5

Table S4. The cathodic peak current and reduction potential at cathodic peak current of M, TaS_2 or its derivatives (TaS_2-PEG, TaS_2-PEG-GR) solution and mixture of two components in the absence and presence of NAD^+

Sample	Reduction potential at cathodic peak current (V)	Cathodic peak current (μA)
M	-0.70	-8.44
TaS_2	-0.90	-11.28
TaS_2+M	-0.82	-11.41
TaS_2+M+NAD^+	-0.80	-19.04
TaS_2-PEG	-0.91	-11.03
TaS_2-PEG+M	-0.83	-11.63
TaS_2-PEG+M+NAD^+	-0.82	-20.21
TaS_2-PEG-GR	-0.92	-11.21
TaS_2-PEG-GR+M	-0.81	-12.25
TaS_2-PEG-GR+M+NAD^+	-0.83	-22.91
TaS_2-PEG-GR-M	-0.81	-13.87
TaS_2-PEG-GR-M+NAD^+	-0.87	-32.03