

## Supporting Information

### **Design and construction of artificial photoresponsive protocells capable of converting day light to chemical energy**

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**Abstract:** We present a new strategy for the design and construction of artificial photoresponsive protocells based on the encapsulation and activation of metallized peptide/porphyrin self-assembled nanofilaments within silica nanoparticle-stabilized colloidosomes. The protocells exhibit high light sensitivity and can utilise day light (700 lux) for the production of nicotinamide adenine dinucleotide (NADH) by photo-mediated reduction of NAD<sup>+</sup> within the colloidosomes. The results provide a promising step towards artificial photosynthetic micro-compartmentalized devices with integrated functional structures and photoresponsive behaviour.

#### **1. Chemicals**

Ac-IIIKK-NH<sub>2</sub> (I<sub>4</sub>K<sub>2</sub>) was provided by Gel BioChem Ltd (Shanghai, China). Tetrakis(4-sulfonatophenyl)porphine (TPPS), nicotinamide adenine dinucleotide (NAD<sup>+</sup> and NADH), L-ascorbic acid, triethanolamine (TEOA), potassium tetrachloroplatinate (K<sub>2</sub>PtCl<sub>4</sub>), dodecane and tetraethoxysilane (TEOS) were purchased from Sigma-Aldrich. Methyl-modified silica nanoparticles with diameters of 20-30 nm (50% silanol groups) were obtained from Wicker Silicons. All chemicals were used as received. All water used was from a Millipore water

purification system with a minimum resistivity of 18.2 M $\Omega$ .

## **2. Characterization methods**

UV-vis spectra of samples were recorded on a PerkinElmer Lambda 25 spectrophotometer with a quartz cuvette and 1 cm path length. Circular dichroism (CD) spectra were obtained on a JASCO J-815 spectrometer with a quartz cuvette and 1 mm path length, and each spectrum was the average of three measurements. Fluorescence spectra were obtained on a Hitachi F-4500 spectrometer. To obtain TEM images, samples were dropped onto the surface of carbon-coated copper grids and dried in air, and examined using JEOL TEM 1400 operated at 120 kV. High resolution images were obtained on JEOL 2100 UHR TEM operated at 200 kV. Optical and fluorescence microscopies were performed on a Leica DMI3000 B manual inverted fluorescence microscope at 40 $\times$  magnifications. A fluorescence filter with excitation at 380-410 nm and 450-490 nm was used. Measurements of photoelectrical responses were performed on a CHI 660E potentiostat/galvanostat electrochemical analyzer using a three-electrode system consisting of an indium tin oxide (ITO) anode covered with the sample, a platinum wire, and a Ag/AgCl electrode. The ITO glass and mounted sample acted as the working electrode, the platinum wire as the counter electrode, and the Ag/AgCl electrode as the reference electrode. The working electrode was prepared on cleaned indium–tin oxide (ITO) glasses, in which a slurry of TPPS, I<sub>4</sub>K<sub>2</sub>/TPPS/Pt or I<sub>4</sub>K<sub>2</sub>/TPPS (both containing the same content of TPPS) was dropped on the glass and dried in air. The surface of the working electrode was a square film with the surface area of 1 cm<sup>2</sup>. The supporting electrolyte was 1 M Na<sub>2</sub>SO<sub>4</sub> containing 0.5% L-ascorbic acid as electron donator. The light was generated by a 300 W xenon lamp (CEL-HXUV300) with a 420 nm cut-off filter.

## **3. Experimental methods**

### **3.1 Preparation of I<sub>4</sub>K<sub>2</sub>/TPPS nanofilaments**

I<sub>4</sub>K<sub>2</sub> was dissolved in ultrapure water to form a solution of 16 mM and kept at room temperature for at least one week to enable peptide nanofilament self-assembly. A known amount of TPPS was mixed with water and slowly added dropwise under stirring into the preassembled I<sub>4</sub>K<sub>2</sub> nanofilament dispersion, and the solution pH then were adjusted to 2.5 by using 0.1 M of HCl

or NaOH solution to give final concentrations of TPPS and I<sub>4</sub>K<sub>2</sub> of 50 μM and 2 mM, respectively.

### **3.2 Preparation of the I<sub>4</sub>K<sub>2</sub>/TPPS/Pt nanofilaments**

A known quantity of K<sub>2</sub>PtCl<sub>4</sub> was dissolved in water at a concentration of 20 mM, and aged for at least 24 hours to form an equilibrium mixture of Pt(H<sub>2</sub>O)<sub>2</sub>Cl<sub>2</sub>, Pt(H<sub>2</sub>O)Cl<sub>3</sub><sup>-</sup> and PtCl<sub>4</sub><sup>2-</sup> [Colombi Ciacchi, L.; Pompe, W.; De Vita, A. *J. Am. Chem. Soc.* **2001**, *123*, 7371]. 0.45 mL of a I<sub>4</sub>K<sub>2</sub>/TPPS nanofilament aqueous suspension, 25 μL of the aged K<sub>2</sub>PtCl<sub>4</sub> solution (20 mM) and freshly prepared L-ascorbic solution (0.2 M, 25 μL) were mixed together, and irradiated with visible light (35000 lux) for 30 min to produce the I<sub>4</sub>K<sub>2</sub>/TPPS/Pt nanofilaments. A control experiment consisting of unbounded Pt nanoparticles was undertaken using a similar procedure but with TPPS solution (50 μM, pH 2.5) in place of the I<sub>4</sub>K<sub>2</sub>/TPPS nanofilaments.

### **3.3 Construction of the artificial photoresponsive protocells**

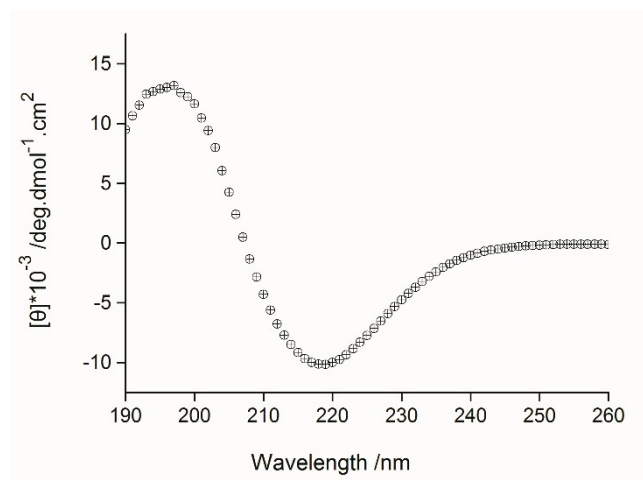
20 mg of methyl-modified silica nanoparticles were dispersed in 2 mL dodecane, and 100 μL of an aqueous dispersion of I<sub>4</sub>K<sub>2</sub>/TPPS/Pt nanofilaments added. Mechanical homogenization was carried out at 10000 rpm for 30 seconds to facilitate the formation of water-in-oil Pickering emulsions. 30 μL of TEOS was then introduced into the oil phase of the Pickering emulsion as a nanoparticle crosslinker, and the sample rotated for 3 days at room temperature. Transfer of the crosslinked Pickering emulsion droplets from the oil phase into water was undertaken as follows. Samples were left unstirred for 1 h, and the upper dodecane layer removed. A mixture of ethanol and water (7:1 v/v) was then added with stirring, and the supernatant removed. This procedure was repeated with increasing water content in the mixture until the colloidosomes were dispersed in pure water.

### **3.4 Regeneration of NADH**

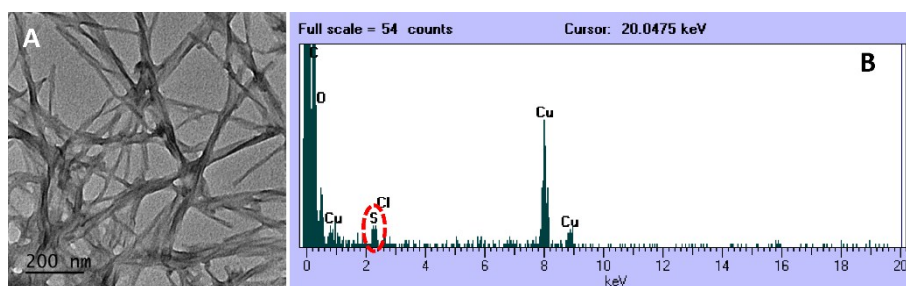
100 μL of I<sub>4</sub>K<sub>2</sub>/TPPS/Pt-containing colloidosomes were mixed with 100 μL of 10 mM aqueous solution of NAD<sup>+</sup> and 150 mg triethanolamine (TEOA), and made up to 1000 μL in the dark and divided into 10 samples that were exposed to a 35000 lux light source (OSRAM 300 W) or to day light (700 lux). In each case, aliquots were removed at intervals of 10-20 min,

centrifuged at 5 krpm for 5 min, and the supernatant monitored for NADH generation by UV-vis spectroscopy (340 nm absorption band). Possible release of  $I_4K_2$ /TPPS/Pt nanofilaments into the bulk solution due to adventitious fragmentation of small numbers of colloidosomes during transfer from oil to water was minimized by allowing the cross-linked water-in-water colloidosomes to settle for 30 min, and then discarding the supernatant. Water was then added to the colloidosomes to increase the volume to 500  $\mu$ L prior to experiments on photo-mediated regeneration of NADH.

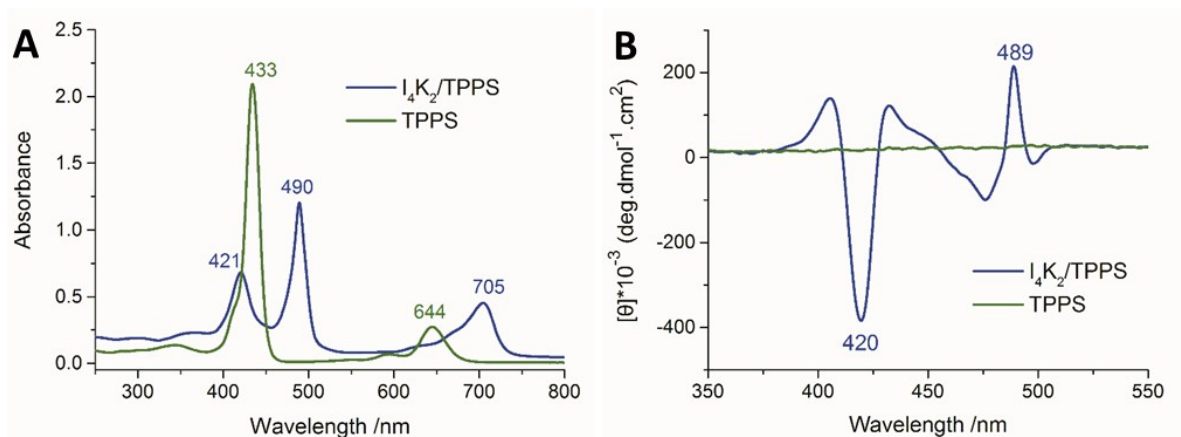
## Supplementary Figures



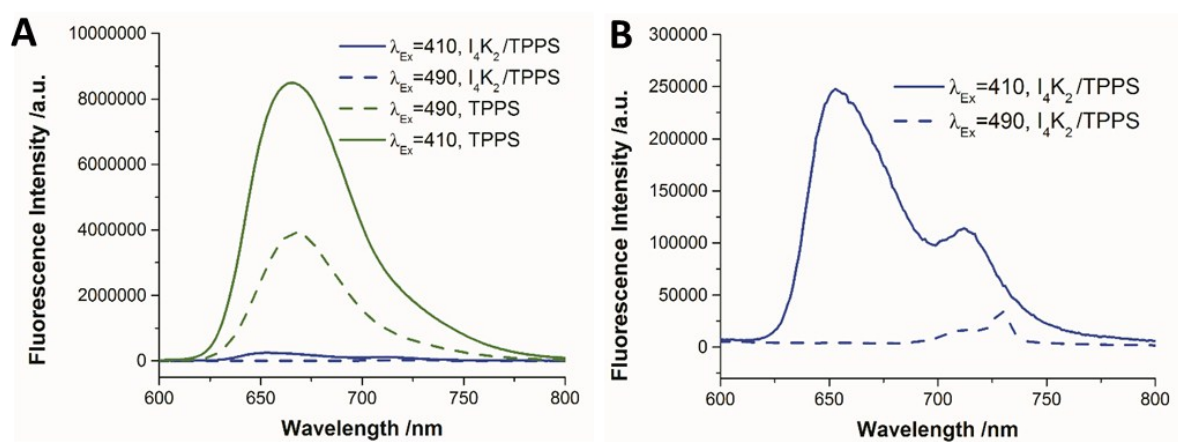
**Figure S1.** CD spectrum of  $I_4K_2$  in aqueous solution showing typical  $\beta$ -sheet profile.



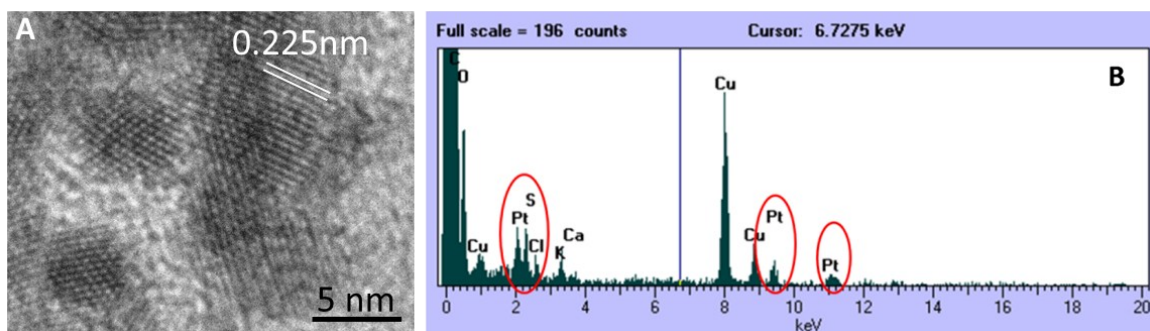
**Figure S2.** TEM image (A) and corresponding energy-dispersive X-ray (EDX) profile (B) of  $I_4K_2$ /TPPS co-aggregates showing the presence of S at 2.3 keV.



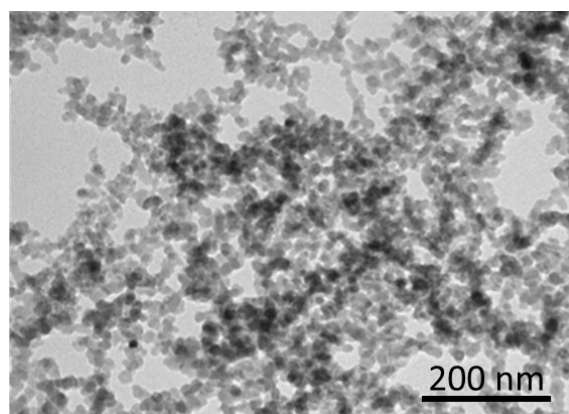
**Figure S3.** UV-vis spectra (A) and CD spectra (B) of TPPS and  $I_4K_2/TPPS$  nanofilaments at pH 2.5.



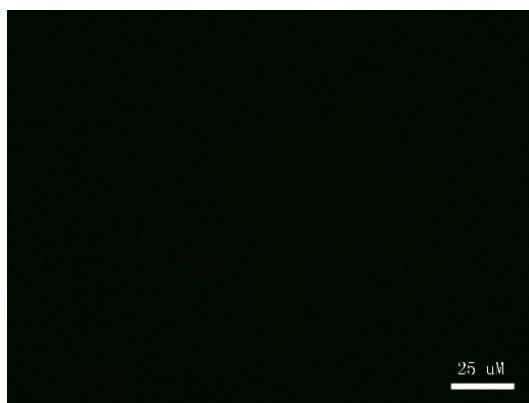
**Figure S4.** (A) Fluorescence spectra of TPPS monomers (control) and  $I_4K_2/TPPS$  nanofilaments excited at 410 and 490 nm showing quenching of peaks for the nanofilaments, consistent with formation of TPPS J-aggregates. (B)  $I_4K_2/TPPS$  spectra for nanofilaments excited at 410 nm and 490 nm plotted on an expanded fluorescence intensity scale.



**Figure S5.** High resolution TEM image (A) and corresponding energy-dispersive X-ray (EDX) profile (B) of  $I_4K_2$ /TPPS/Pt nanofilaments showing (111) lattice planes with interplanar spacing of 0.225 nm, and presence of Pt, respectively.

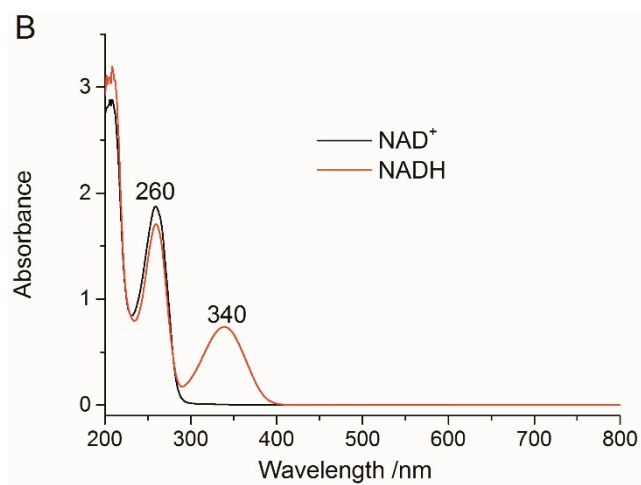
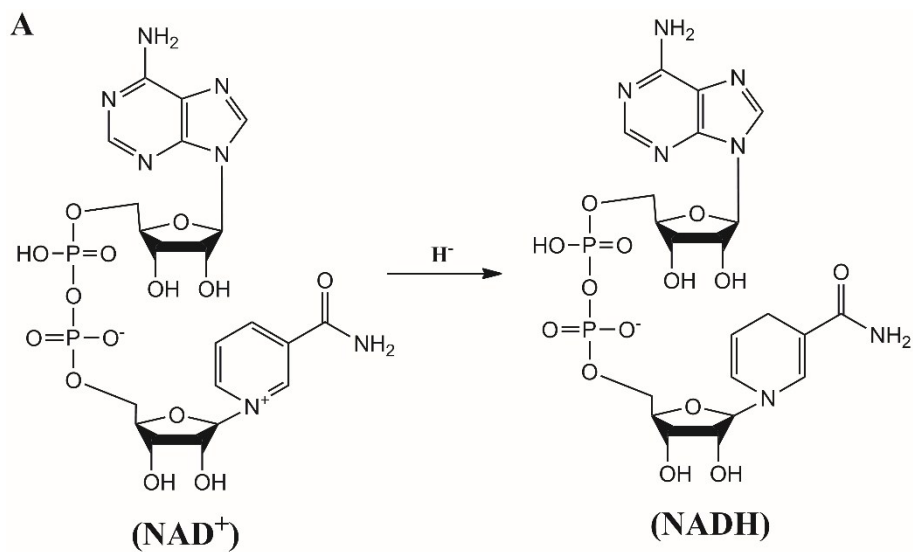


**Figure S6.** TEM image of silica nanoparticles used for the construction of colloidosomes.

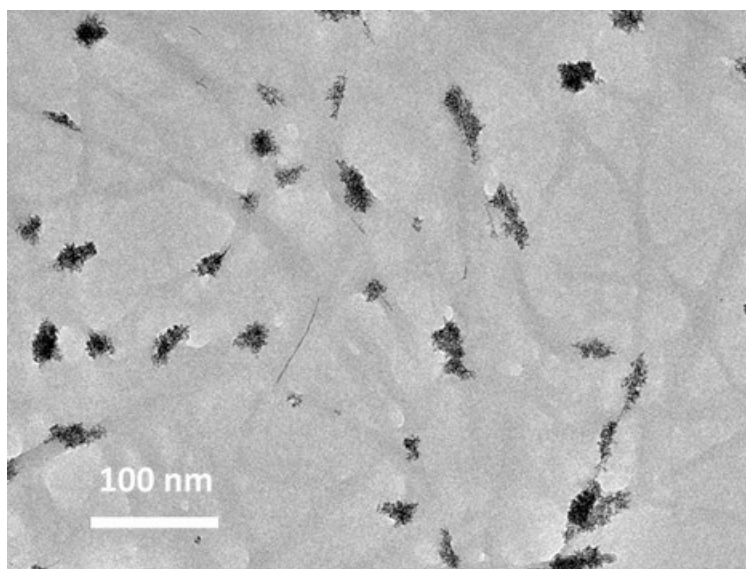


**Figure S7.** Fluorescence microscopy image of I<sub>4</sub>K<sub>2</sub>/TPPS/Pt-containing colloidosomes recorded at an excitation wavelength of 450-490 nm. The absence of fluorescence was consistent with the presence of J-aggregates within the protocells.

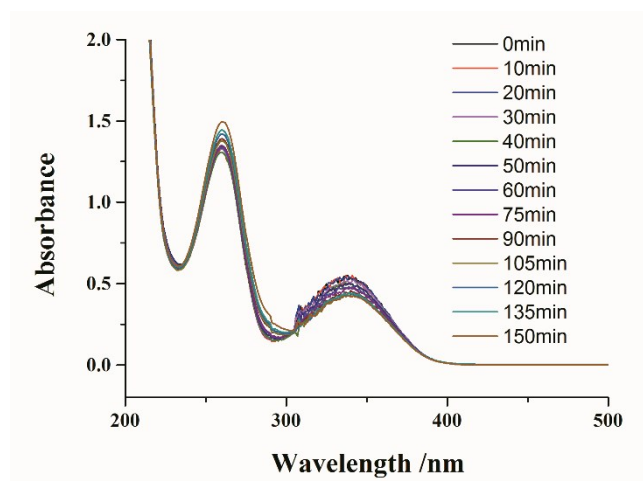




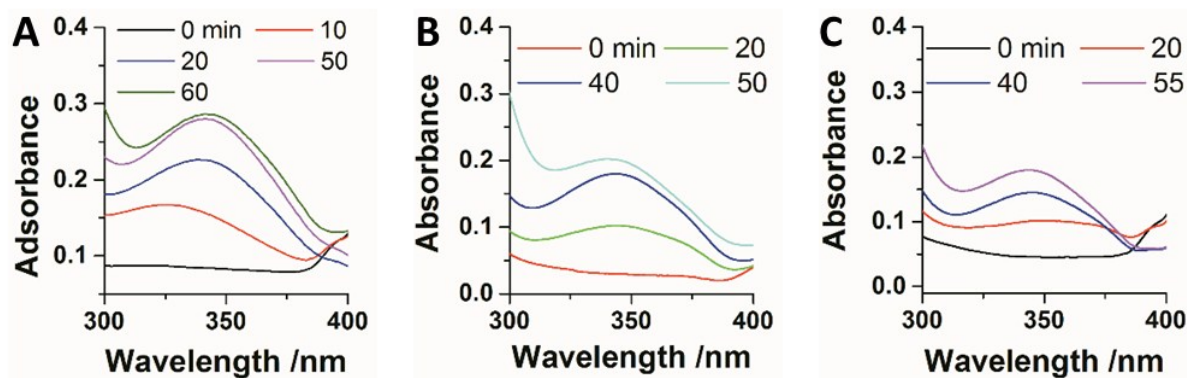
**Figure S8.** Chemical structures (A) and UV-vis spectra (B) of NAD<sup>+</sup> and NADH.



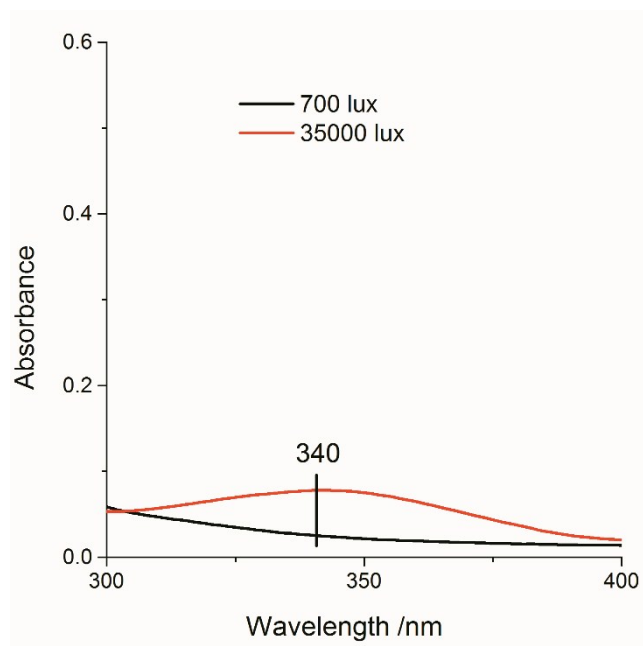
**Figure S9.** TEM image of the  $I_4K_2$ /TPPS/Pt complex after 1 hour of irradiation at 35000 lux.



**Figure S10.** UV-vis spectra of NADH solution (1mM) irradiated (35000 lux) for different periods of time. The peak intensities at 340 and 260 nm decreased and increased with time indicating that high light intensity accelerated the oxidation of NADH to  $NAD^+$ .



**Figure S11.** UV-vis spectra recorded during the generation of NADH in the presence of  $I_4K_2$ /TPPS/Pt (A),  $I_4K_2$ /TPPS (B), and TPPS (C). Note that the reactions are carried out under 35000 lux irradiation and with the same TPPS concentration for all the reaction systems.



**Figure S12.** UV-vis spectra of photo-mediated NADH generation for 60 min in the presence of free (unbound) Pt nanoparticles and water-soluble TPPS under 35000 lux light (red profile) or day light (700 lux, black profile).