Supporting Information

Plasmon-driven photoregeneration of cofactor molecules

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1. Methods

1. Materials. Tetrachloroauric acid ($HAuCl_4 \bullet 3H_2O$), potassium tetrachloro- platinate(II) (K_2PtCl_4), cetyltrimethylammonium bromide (CTAB), ascorbic acid, sodium borohydride ($NaBH_4$), hydrochloric acid (HCl), $AgNO_3$, sodium citrate monohydrate, NAD^+ , NADH, triethanolamine (TEA) were purchased from Aldrich and used as received. Milli-Q water with a resistivity higher than 18.2 MΩ cm was used in all of the preparations. Corning Glass was as a substrate for plasmonic nanoparticles.

2. Synthesis of gold nanorods (AuNRs). Gold nanorods were prepared using Ag-assisted seeded growth.[1] Seeds were prepared by reduction of $HAuCl_4$ (0.25 mM, 5 mL) with $NaBH_4$ (10 mM, 0.3 mL) in aqueous CTAB solution (100 mM). An aliquot of seed solution (240 μL) was added to a growth solution (100 mL) containing CTAB (100 mM), $HAuCl_4$ (0.5 mM), ascorbic acid (0.8 mM), $AgNO_3$ (0.12 mM), and HCl (19 mM). The mixture was left undisturbed at 30 °C for 2h.

3. Synthesis of tip-functionalized gold nanorods. The platinum reduction on the tips of gold nanorods have been described in detail in previous work.[2] Briefly, the growth solution (50 mL) that contained as–prepared gold nanorods (0.5 mM), H_2PtCl_4 (0.025 mM) and ascorbic acid (0.5 mM) was was left undisturbed for 12 hours at 40 ºC.

4. Fabrication of plasmonic substrates
As prepared AuNRs@Pt (0.5 mM, 50 mL, [CTAB] = 0.1 M) were centrifuged and redispersed in CTAB (1 mM, 2 mL). The solution was again centrifuged and redispersed in pure water (1 mL). Parafilm was used to wrap the edges of the glass substrate (0.8 x 2.5 cm) to produce a container. The solution of nanoparticles was then placed in the container and evaporated at room temperature during 3 days.

5. Photocatalytic regeneration of NAD^+ on plasmonic substrate containing AuNR@Pt.
Plasmonic substrate was immersed in photochemical mixture (1 mL, in quartz cuvette) consisting of phosphate buffer (0.1 M, pH 8), NAD^+ (1 mM) and TEA (1M). The cuvette was irradiated with

visible/infrared light (MI-150 High-Intensity Illuminator). After a desire time the plasmonic substrate was removed from the cuvette and the solution was analyzed by UV-Vis spectroscopy. The concentration of NADH was determined based on absorption band intensity at 340 nm.

6. Photocatalytic regeneration of NAD^+ on AuNRs@Pt in colloidal phase
The solution of AuNRs@Pt (3 mL, 10mol% Pt, [Au] = 1.5 mM, [CTAB] ~3 mM) containing phosphate buffer (0.1 M, pH 8), TEA (1M) and NAD^+ (1mM) was placed in quartz cuvette and irradiated with visible/infrared light. After each 15 minutes of irradiation, 0.1 mL of the solution was diluted to 1 mL with water and was centrifuged to remove nanoparticles. The supernatant was analysed by UV-Vis spectroscopy. The concentration of NADH was determined based on absorption band intensity at 340 nm.

7. *Preparation of bulk gold film.* Au films with thickness of ~200 nm were deposited on glass substrates with magnetron sputtering using an AJA-ATC 1800 system with a base pressure of 10-7 Pa. The deposition of the films was done with a 2-inch Au target, (99.99% purity) at a d.c. power of 150 W and a pressure of 0.4 Pa of pure Ar. The films were grown under floating potential and at room temperature. The distance between target and substrates was about 15 cm. Prior to deposition; the substrates were sputter cleaned with a negative bias of 180 V (25 W) in a 4 Pa Ar atmosphere for 3 min. In order to improve the adhesion of the Au films to the glass substrates, a pure Ti layer of ~1 nm was deposited onto the substrates from a pure 2-inch Ti target (99.995% purity) at a d.c. power of 230 W and a pressure of 0.4 Pa of pure Ar. The as-prepared gold film was immersed in the CTAB solution (0.1 M) containing K_2PtCl_4 (0.5 mM) and ascorbic acid (10 mM) and kept undisturbed for 12 hours. Prior photochemical reaction the substrate was washed with water and ethanol and dried under argon flow.

2. Characterization

UV-Vis spectra were collected using a scanning spectrophotometer Agilent 8453 UV/Vis diode-array spectrophotometer. Transmission electron microscopy (TEM) images were collected with a JEOL JEM-1400PLUS, operating at 120 kV. Scanning electron microscopy (SEM) images were collected with Scanning electron microscopy (SEM) was measured with a dual beam FIB - FEI Helios 450S microscope with electron column resolution of 0.8 nm at 20 kV. 1H NMR spectra of the various samples were recorded in D_2O on an AVANCE III Bruker 500 NMR spectrometer.

3. Regeneration of NAD⁺ on AuNRs@Pt in colloidal phase.

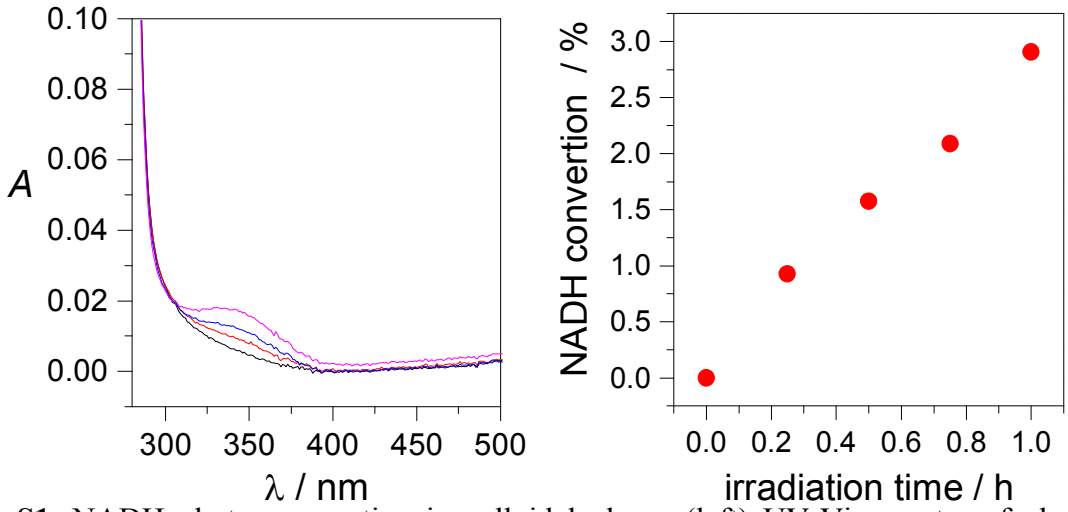

Figure S1. NADH photoregeneration in colloidal phase. (left) UV-Vis spectra of photoreduced NADH at different reaction time. (right) The rate of the NADH reduction, obtained from UV-Vis characterization.

4. Low resolution SEM

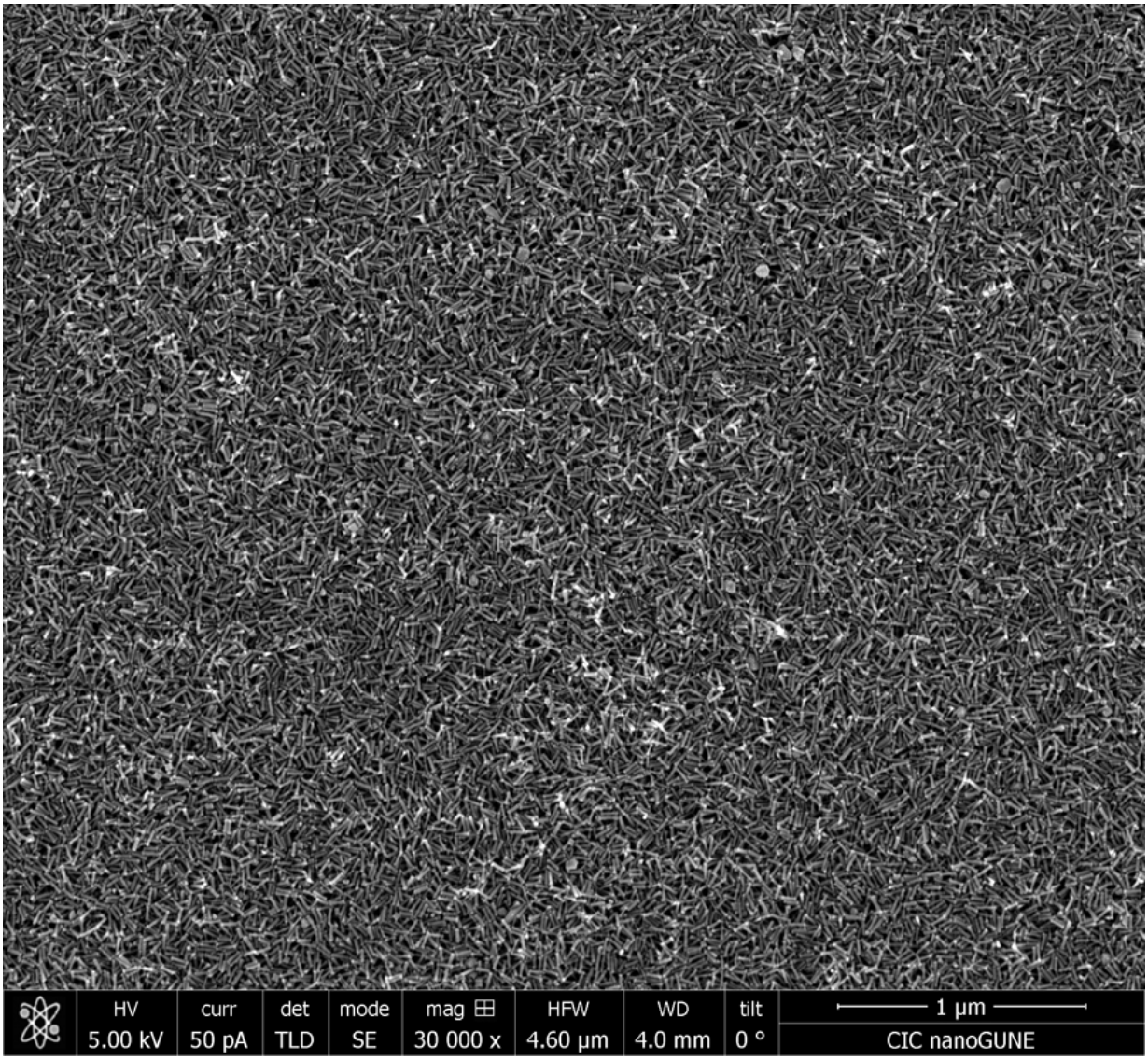

Figure S2. Top view of typical plasmonic substrate containing AuNRs@Pt showing homogeneous distribution of the nanoparticles.

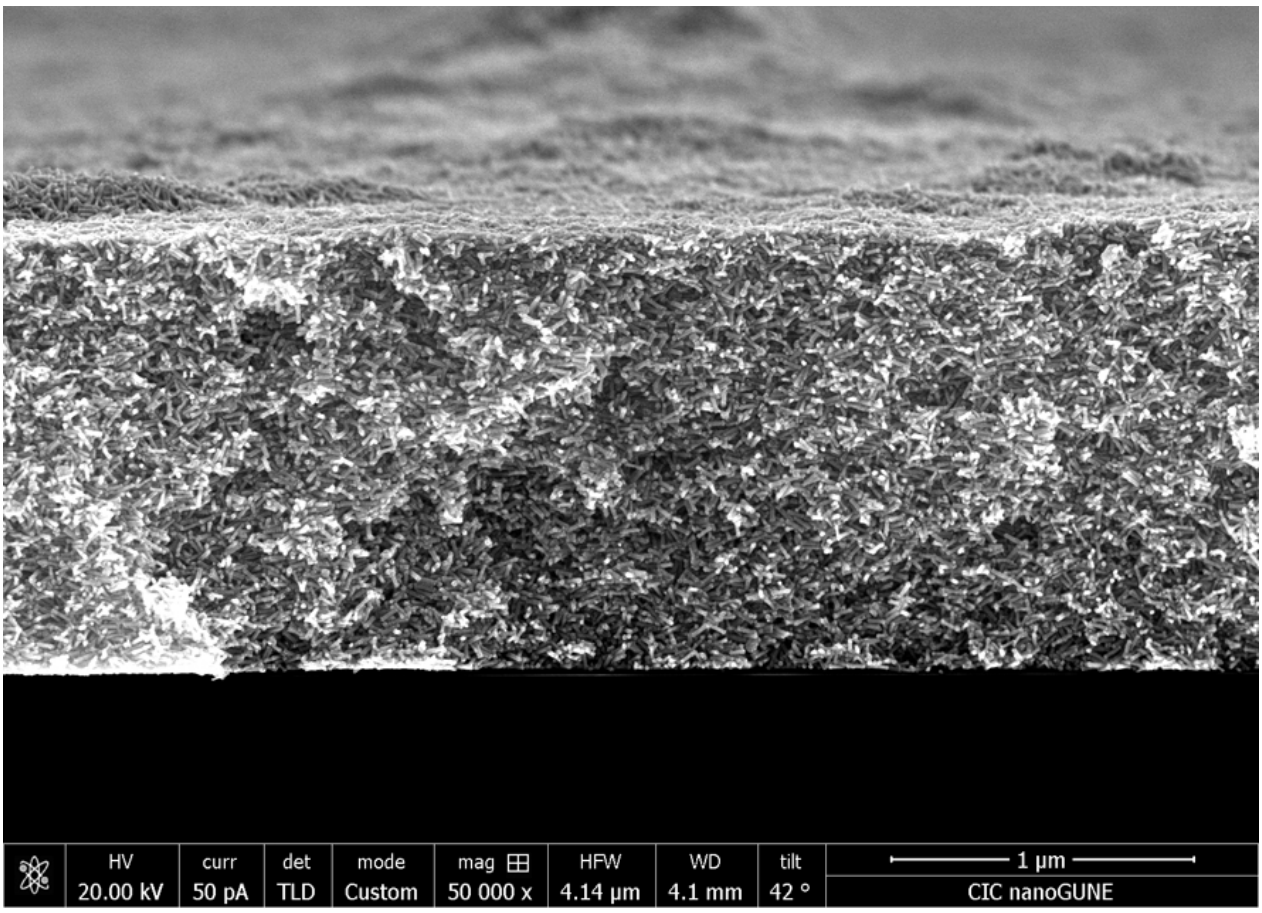

Figure S3. Side view of typical plasmonic substrate.

5. NMR characterization of photo-regenerated NADH

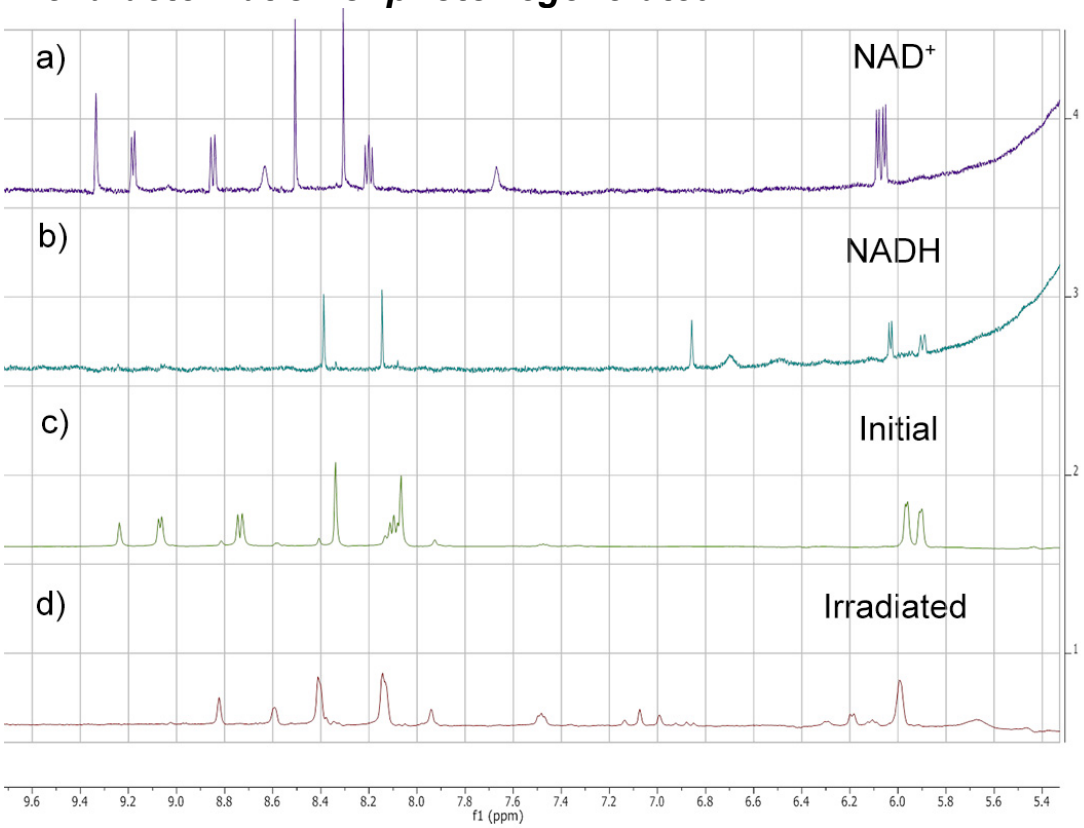

Figure S4. Evidence of NAD^+ regeneration. (a,b) NMR spectra of solution containing oxidized and reduced cofactor, respectively. (c, d) NMR spectra of mixtures containing NAD^+ and TEA before and after photochemical reaction.

6. The spectral characteristics of the light source used.

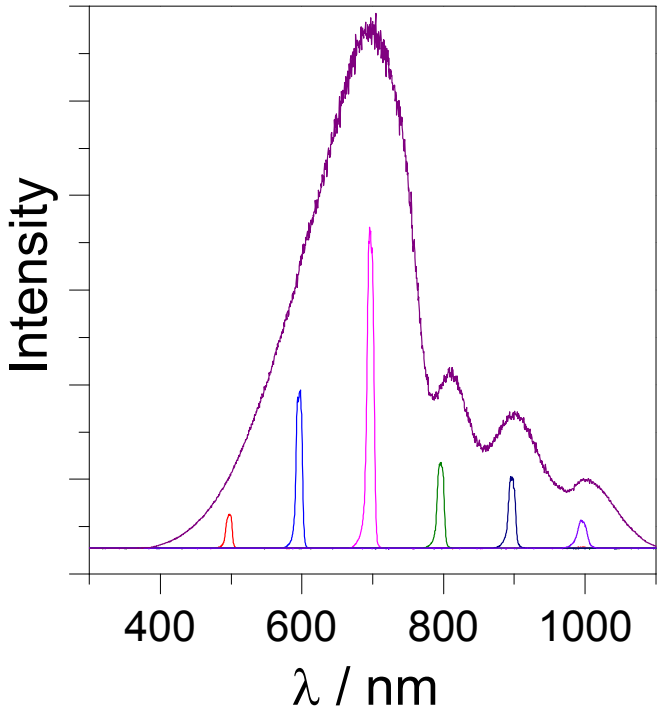

Figure S5. Spectra profile of the light source used in our experiments. The individual peaks correspond to the light intensity with applied bypass filter.

7. Diffusive Reflectance spectra of plasmonic substrates

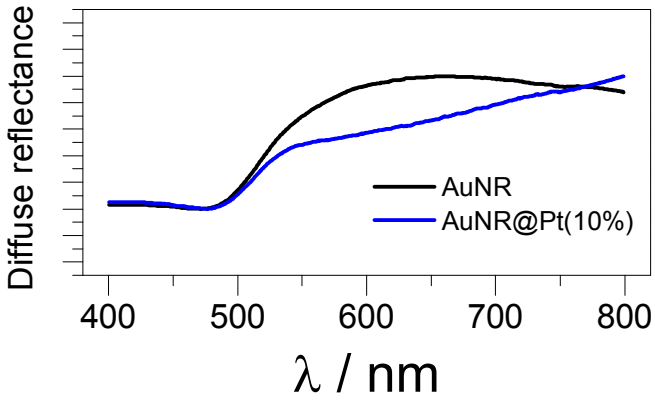

Figure S6. Diffusive reflectance spectra of the plasmonic substrates showing strong reflectance of the particles above 500 nm.

8. Control experiments

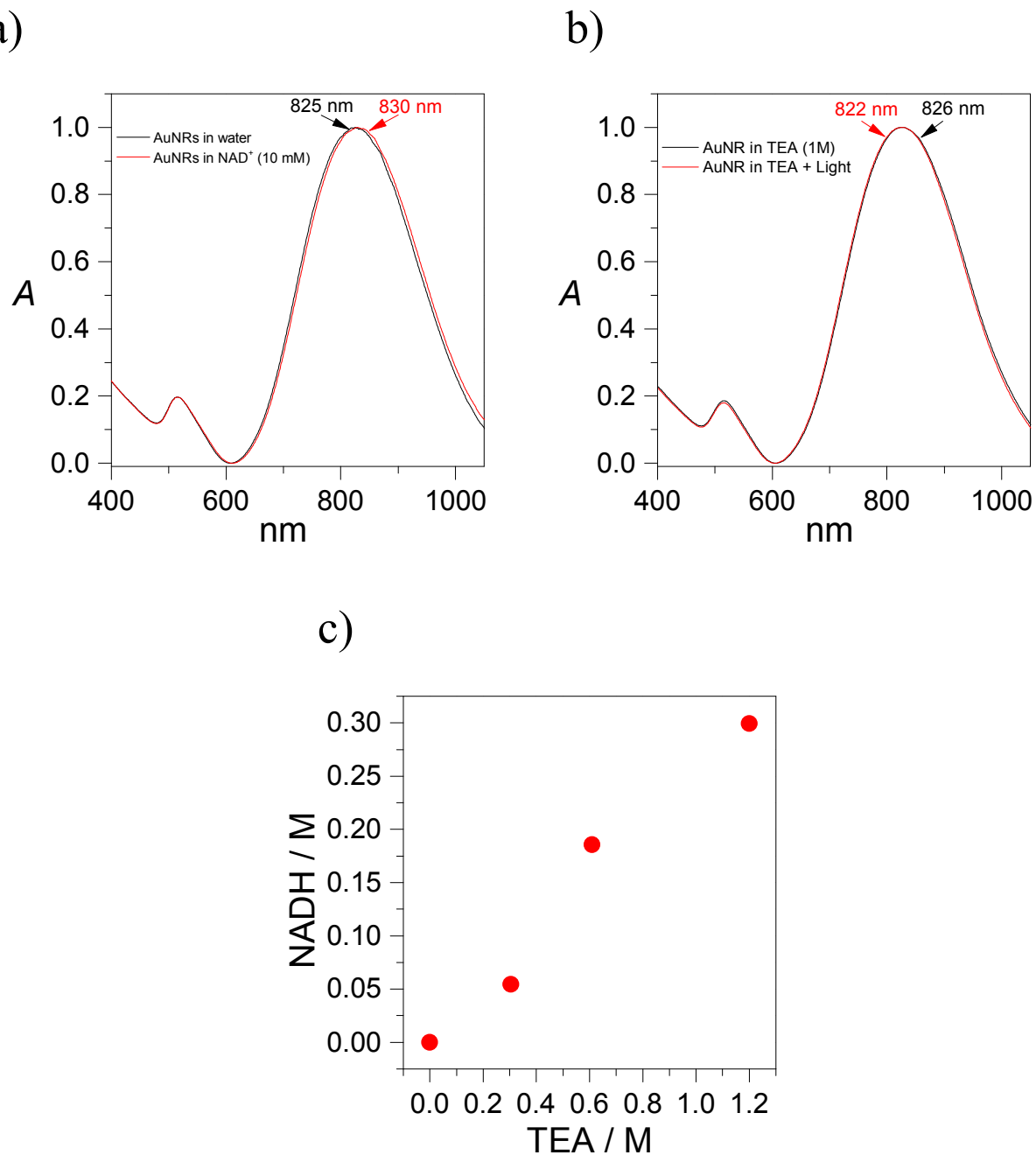

Figure S7. (a) Interaction of NAD^+ with gold surface. UV-Vis-NIR spectra of AuNRs@Pt in the presence of NAD^+ (no TEA) showing slight redshift of the LSPR. (b) UV-Vis-NIR spectra of AuNRs@Pt in the presence of TEA (no NAD^+) showing slight blueshift of the LSPR under light irradiation. (c) The effect of TEA concentration on the final NADH photoregeneration (2 h of irradiation).

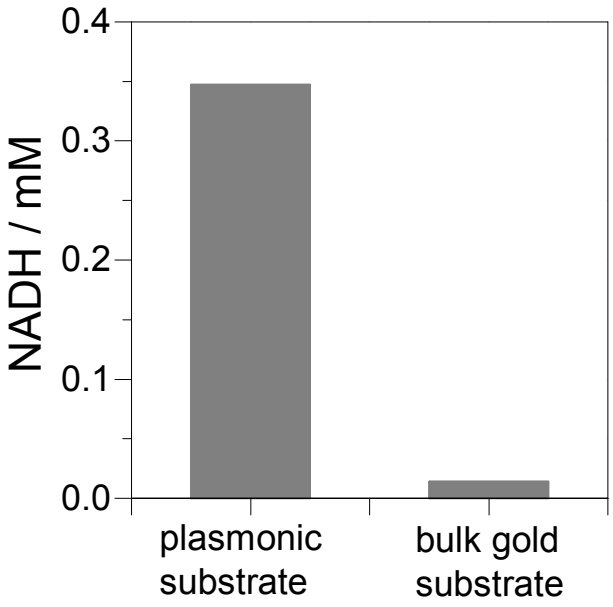

Figure S8. The comparison of NADH photo-regeneration on plasmonic substrate containing AuNRs@Pt and bulk gold film, showing negligible conversion of NADH on bulky gold substrate.

9. References

(1) Liu, M.; Guyot-Sionnest, P. *J. Phys. Chem. B* **2005**, *109*, 22192–22200.
(2) Grzelczak, M.; Perez-Juste, J.; Rodriguez-Gonzalez, B.; Liz-Marzan, L. *J. Mater. Chem.* **2006**, *16*, 3946–3951.