

EXPERIMENTAL METHODS

Materials: Tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate, dichlorotris(1,10-phenanthroline)ruthenium(II) hydrate, potassium tetrachloroplatinate (K_2PtCl_4), L-glutamic dehydrogenase from bovine liver (GDH) and α -Ketoglutaric acid were purchased from Sigma-Aldrich. Tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) dichloride complex, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and nicotinamide adenine dinucleotide (NAD^+) were purchased from Aladdin. Ascorbic acid and triethanolamine (TEOA) were purchased from Sinopharm Chemical Reagent Co. Ltd. Diphenylalanine (Phe-Phe, FF) was purchased from Bachem (Bubendorf, Switzerland). All chemicals were used without further purification.

Synthesis of FF, FF/Ru, and FF/Ru/Pt nanotubes: For the formation of FF/Ru nanotubes, FF was dissolved in HFIP at 100 mg mL^{-1} and diluted with a phosphate buffer (100 mM, pH 6.0), which is containing 1 mg mL^{-1} ruthenium complexes to reach the final concentration of 10 mg/ml. For the corporation with Pt of the nanotubes, FF/Ru nanotubes were redispersed in the phosphate buffer (100 mM, pH 6.0) containing K_2PtCl_4 (7 mM) and ascorbic acid (7 mM). The mixture was irradiated with visible light from a 350 W Xe lamp for 30 minutes. The self-metallized FF/Ru/Pt nanotubes were then isolated by filtration, and dispersed in a phosphate buffer (100 mM, pH 6.0). It is worth mentioning that some of the nanotubes may not be metallized. We did not separate the non-metallized nanotubes from the self-metallized ones. After the self-metallization, all nanotubes were used for photo-catalysis.

Characterization:

X-ray powder diffraction

The structure of lyophilized FF nanotubes was analyzed using a X-ray powder diffractometer (D8 Advance, BRUKER AXS GmbH) under the following conditions: sample amount 0.3-0.5 mg; temperature: 25°C ; scan speed: $0.5^\circ/\text{s}$; CuK α radiation, $\lambda = 1.5418\text{ \AA}$; scan range: $5^\circ - 80^\circ$.

Scanning electron microscope (SEM)

Scanning electron microscopic images and microanalysis reports were obtained using a Quanta Scanning Electron Microscope (Quanta 200, FEI) at 20 kV. The lyophilized samples were analyzed directly without using metal conductive coating.

Transmission electron microscope (TEM)

Transmission electron microscopic images were obtained using a JEM-200CX . The sample solution was dropped on the copper grid and dry under the nitrogen.

UV-Vis spectroscopy

UV-vis spectra of all samples were measured using a V-550 (JASCO Inc., Japan) spectrophotometer. The cuvette width was 1 cm and the bandwidth was set as 0.2 nm.

Fluorescence spectroscopy

Spectrofluorometric experiments were performed using an FP-6500 (JASCO Inc., Japan). The emission spectra were measured using an excitation wavelength of 258 nm. The bandwidth was set as 0.2 nm.

Time-resolved phosphorescence

Time-resolved phosphorescence decays of Ru1, Ru2, Ru3, FF/Ru1, FF/Ru2, and FF/Ru3 (excited at 400 nm) were performed using a PicoHarp300 (TCSPC). The measure interval is 0.008 ns.

Photocurrent

The FF/Ru nanotubes were deposited on an indium tin oxide (ITO) glass in phosphate buffer (100 mM, pH 6.0) containing 15% (w/v) triethanolamine (TEOA) as an electron donor. The photocurrents were measured with an electrochemical workstation under the working voltage of 1.2 V.

Cyclic voltammogram (CV)

A 3-electrode system was used to obtain cyclic and linear sweep voltammograms; glassy carbon (working electrode), Ag/AgCl (reference electrode), and a platinum wire (counter electrode) were connected to a electrochemical workstation with 100 mV/s scan rate.

Visible light-driven NADH regeneration: Photochemical regeneration of NADH was performed in a quartz reactor at room temperature. 1 mM NAD⁺ was dissolved in a phosphate buffer (100 mM, pH 6.0) containing 15 % (w/v) TEOA. The light-harvesting peptide nanotubes (FF /Ru /nPt nanotubes) were dispersed in the reaction solution and exposed to the visible light from a Xe lamp source. The concentrations of NAD⁺ and regenerated NADH were measured according to the absorbance at 260 nm and 340 nm using a spectrophotometer (JASCO Inc., Japan).

Photoenzymatic synthesis of L-glutamate: Photoenzymatic synthesis of L-

glutamate using FF/Ru/Pt nanotubes was conducted in an quartz cuvette, which included 1 mM NAD⁺, 5 mM α -ketoglutarate, 100 mM ammonium sulphate, 50 U GDH, and 15 w/v% TEOA in a phosphate buffer (100 mM, pH 6.0) under the visible light. The concentration of L-glutamate was measured according to the increase in the absorbance of L-glutamate at 214 nm using a spectrophotometer.

Supporting Figures

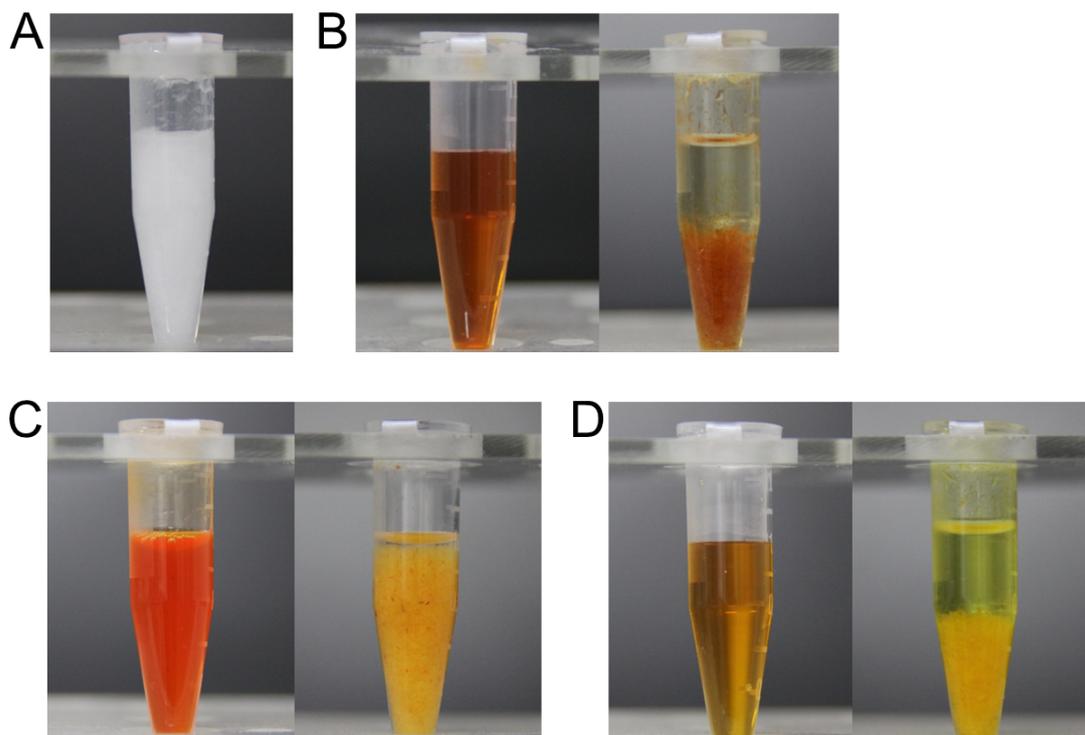


Figure S1 Photographs of microcentrifuge tubes containing FF nanotubes and/or ruthenium complexes. (A) 10 mg mL^{-1} of FF. (B) 1 mg mL^{-1} Ru1 in the absence (left) and presence (right) of 10 mg mL^{-1} of FF. (C) 1 mg mL^{-1} Ru2 in the absence (left) and presence (right) of 10 mg mL^{-1} of FF. (D) 1 mg mL^{-1} Ru3 in the absence (left) and presence (right) of 10 mg mL^{-1} of FF.

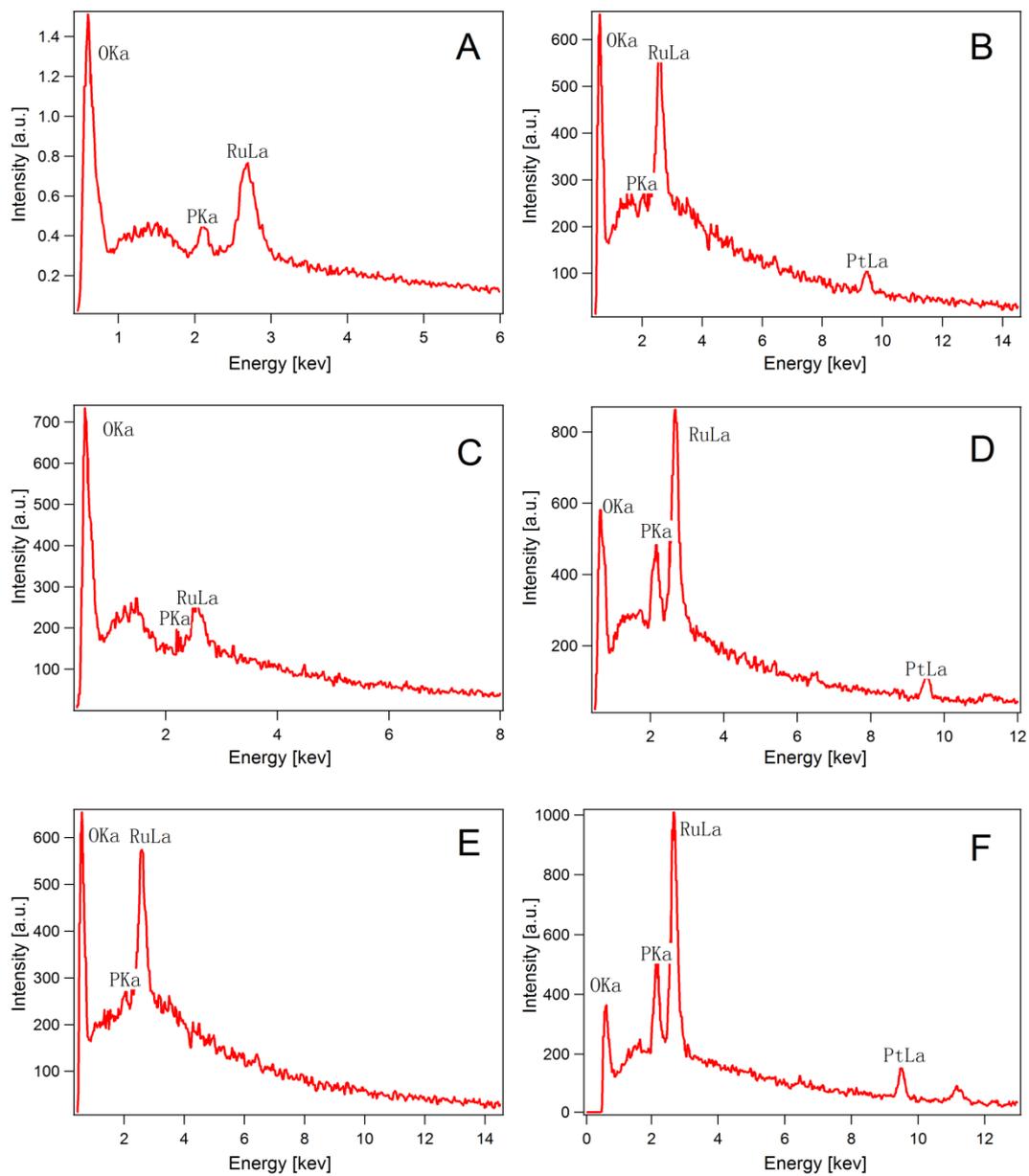


Figure S2 Elemental analysis of FF/Ru nanotubes and FF/Ru/Pt nanotubes. (A) FF/Ru1; (B) FF/Ru1/Pt; (C) FF/Ru2; (D) FF/Ru2/Pt; (E) FF/Ru3; (F) FF/Ru3/Pt.

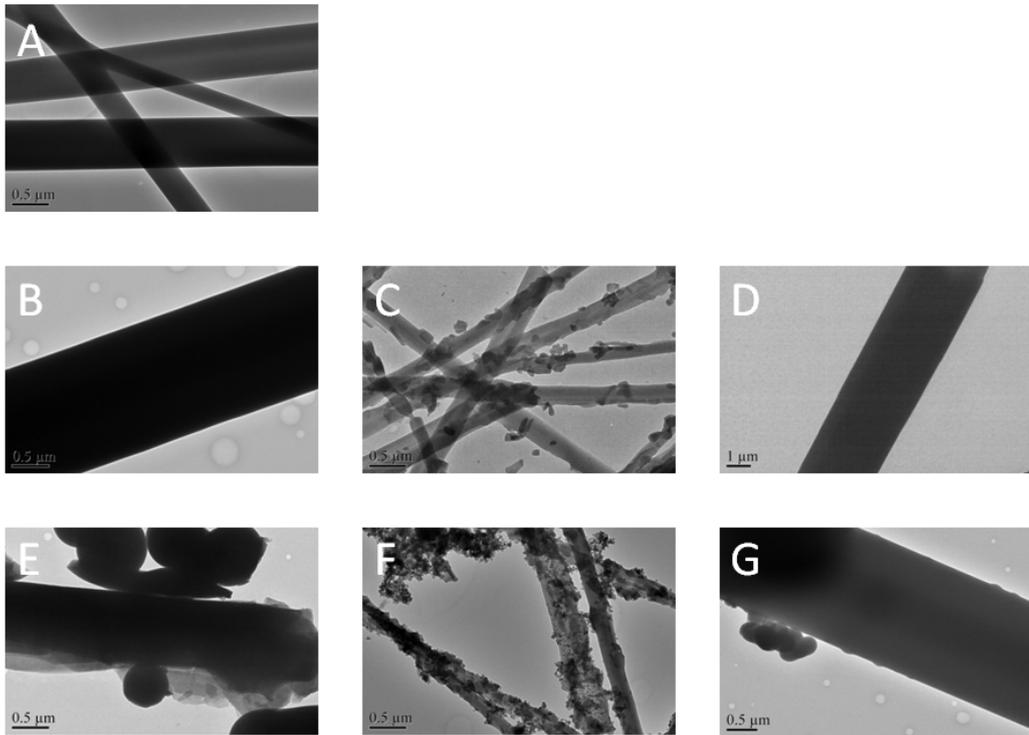


Figure S3 (A)-(G) TEM images of FF, FF/Ru1, FF/Ru2, FF/Ru3, FF/Ru1/Pt, FF/Ru2/Pt, and FF/Ru3/Pt, respectively.

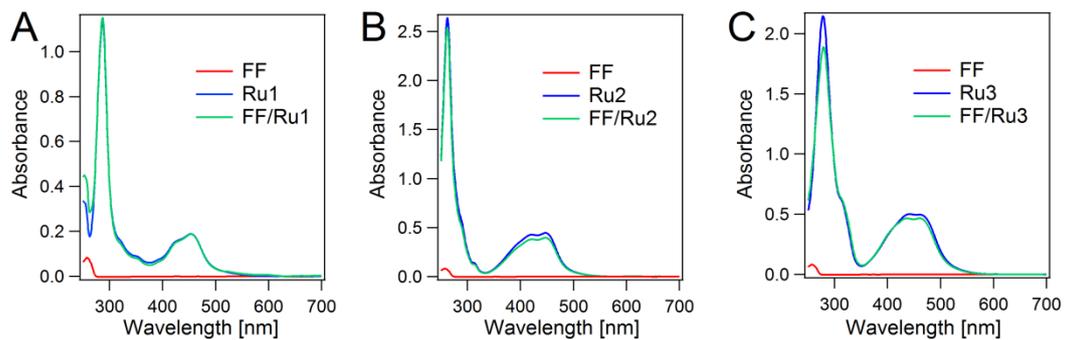


Figure S4 UV-Vis spectra of FF nanotubes, ruthenium complexes, and FF/Ru nanotubes. (FF: 1 mg mL^{-1} ; ruthenium complex: 0.1 mg mL^{-1})

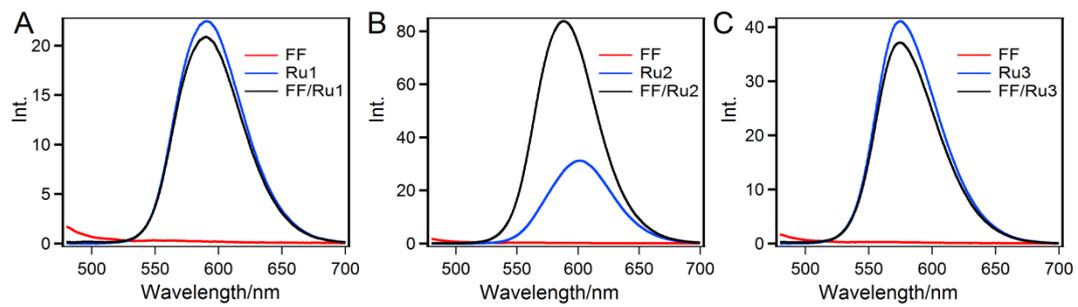


Figure S5 Fluorescence spectra of ruthenium complexes in the absence and presence of FF nanotubes (excited at 440 nm). (FF: 1 mg mL^{-1} ; ruthenium complex: 0.1 mg mL^{-1})

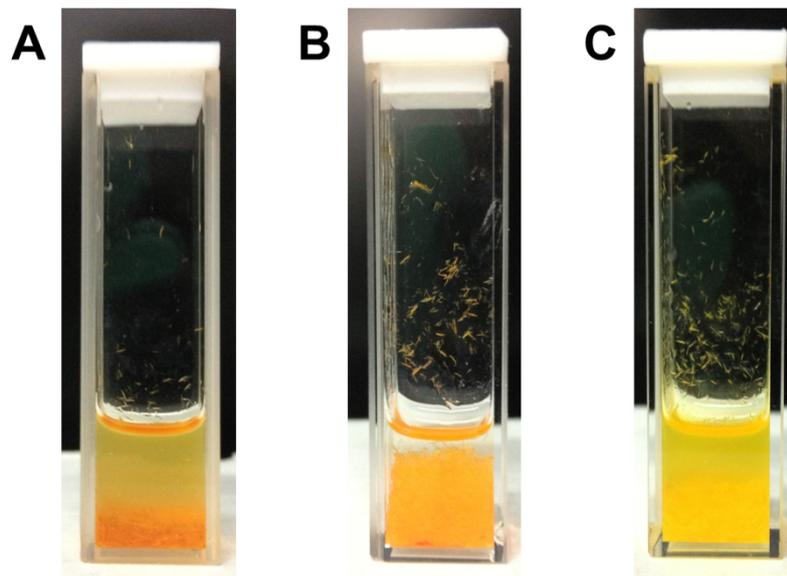


Figure S6 Photographs of FF/Ru/Pt nanotubes (A) FF/Ru1/Pt; (B) FF/Ru2/Pt; (C) FF/Ru3/Pt.

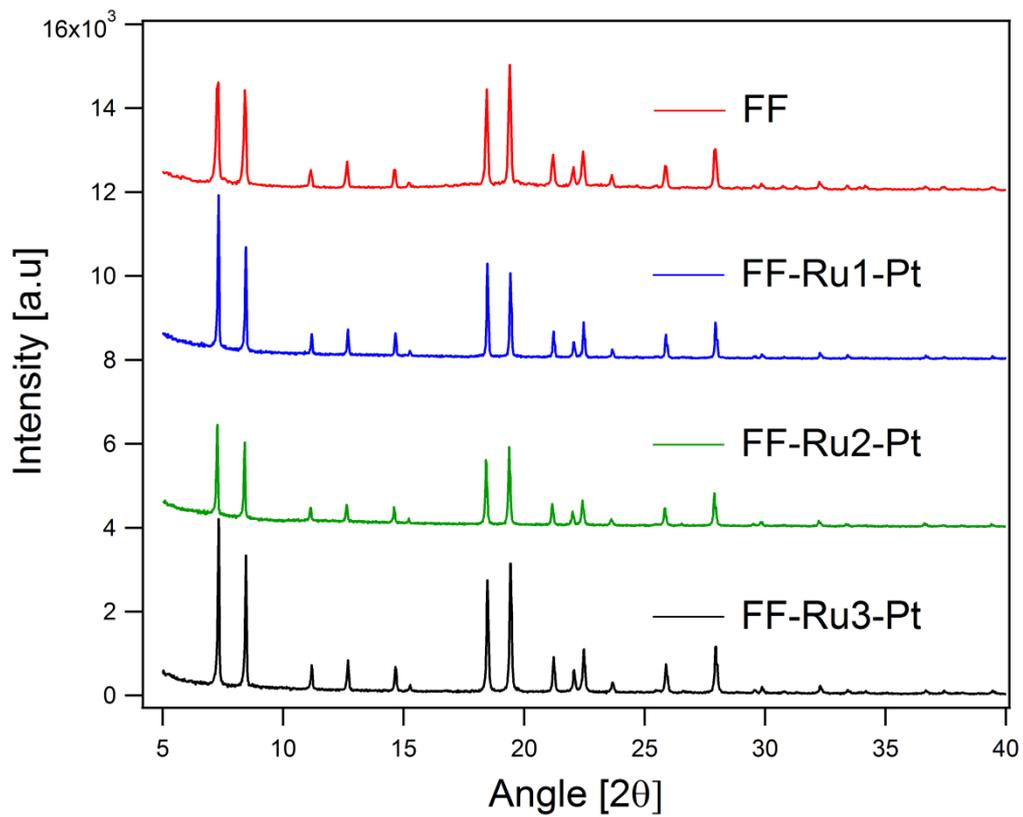


Figure S7 XRD of FF/Ru/Pt nanotubes.

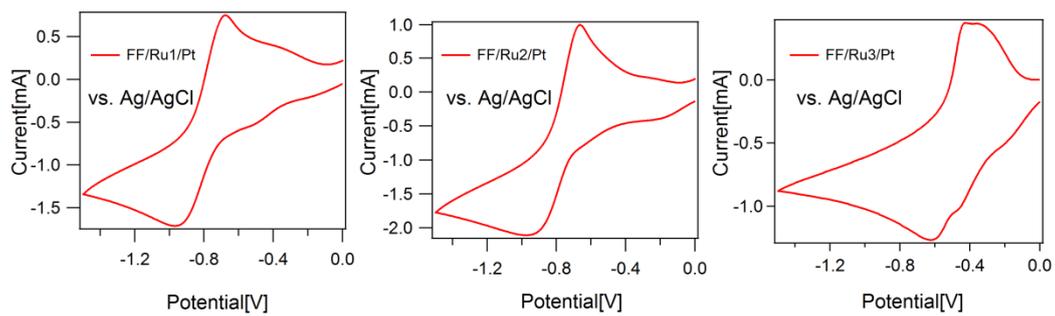


Figure S8 Cyclic voltammogram of FF/Ru/Pt nanotubes with a scan rate of 100 mV s^{-1} .

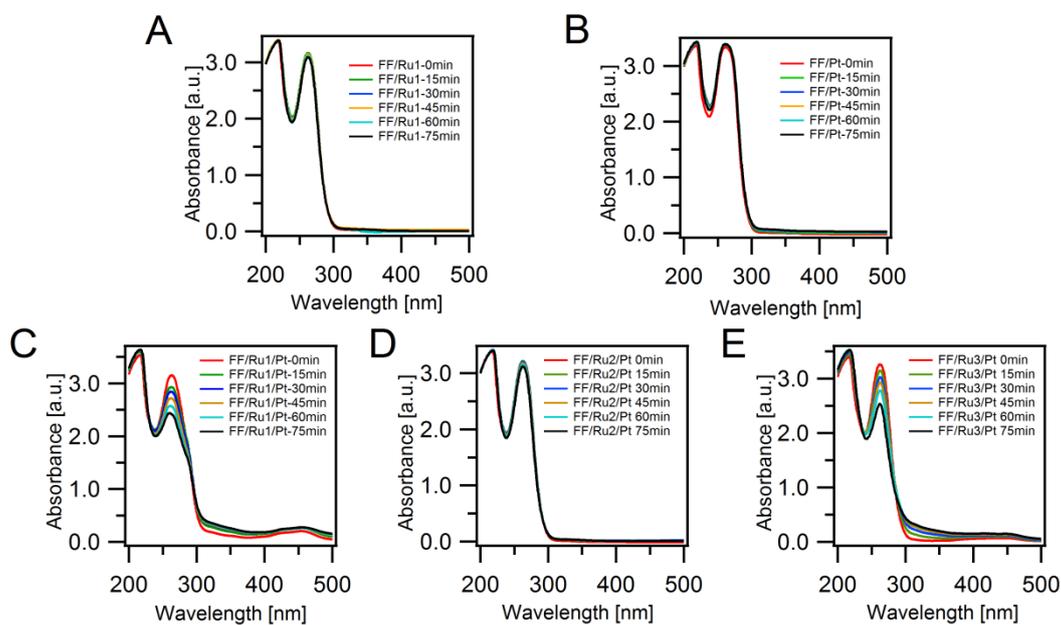


Figure S9 UV-Vis spectra of FF/Ru, FF/Pt and FF/Ru/Pt catalyzed conversion of NAD^+ to NADH . The concentration of initial NAD^+ was 0.53 mg mL^{-1} . The concentrations of FF, Ru, and Pt were 2 mg mL^{-1} , 0.2 mg mL^{-1} , and 0.27 mg mL^{-1} , respectively. (A) FF/Ru1; (B) FF/Pt; (C) FF/Ru1/Pt; (D) FF/Ru2/Pt; (E) FF/Ru3/Pt.

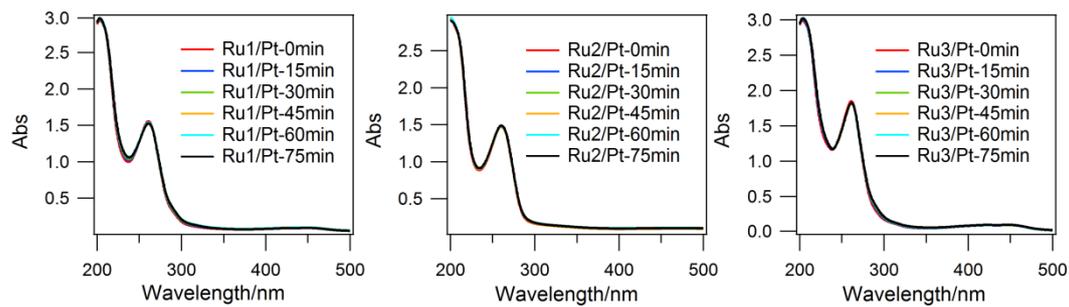


Figure S10 UV-Vis spectra of Ru/Pt catalyzed conversion of NAD⁺ to NADH. The concentrations of initial NAD⁺, FF, Ru, and Pt were 0.177 mg mL⁻¹, 0.67 mg mL⁻¹, 0.067mg mL⁻¹, and 0.09 mg mL⁻¹