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Supporting Information

Photocatalytic hydrogen evolution driven by platinated CdS nanorods with a hexacyanidoruthenate redox mediator

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Contents

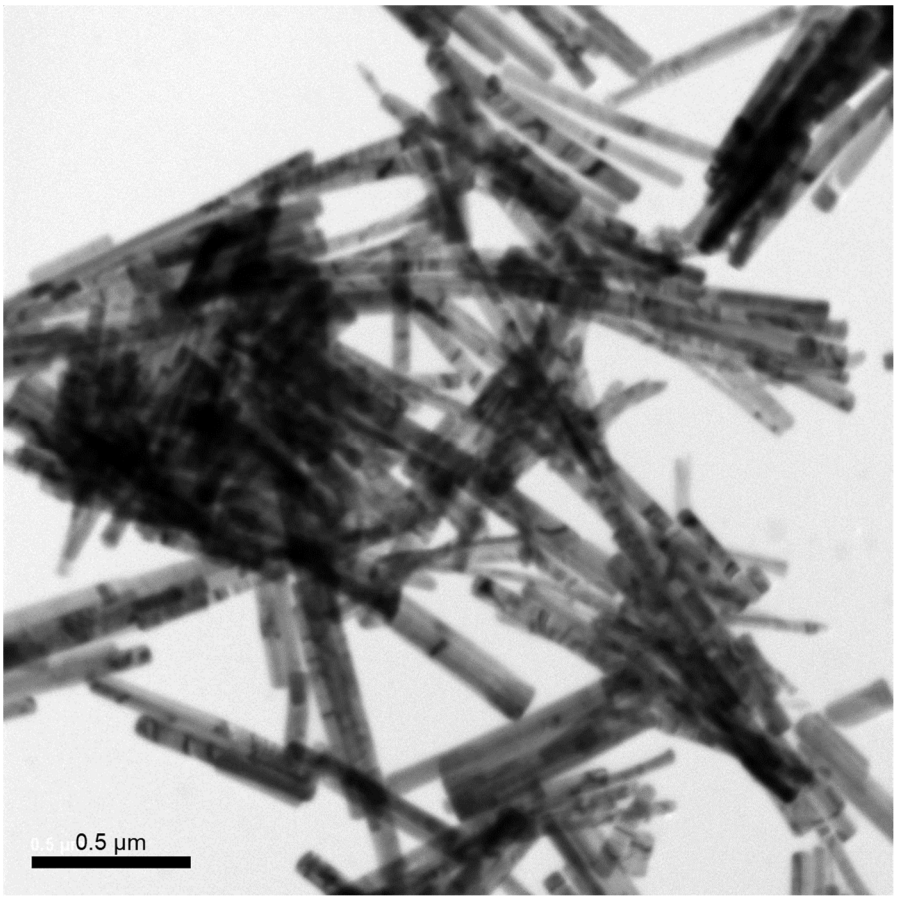

Figure S1. TEM image of the as-prepared Pt/CdS-NR.

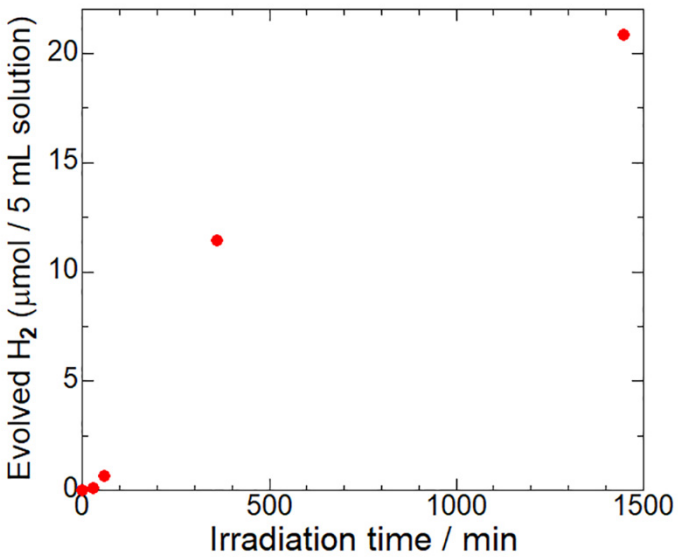

Figure S2. Long-term photocatalytic hydrogen evolution reaction with Pt/CdS-NR (2 mg) in a 200 mM acetate buffer (pH=5.0) which contained the 0.01 M $K_4[Ru(CN)_6]$ as electron sources under Ar atmosphere. A blue LED (λ = 470 ± 10 nm) was used as the light source.

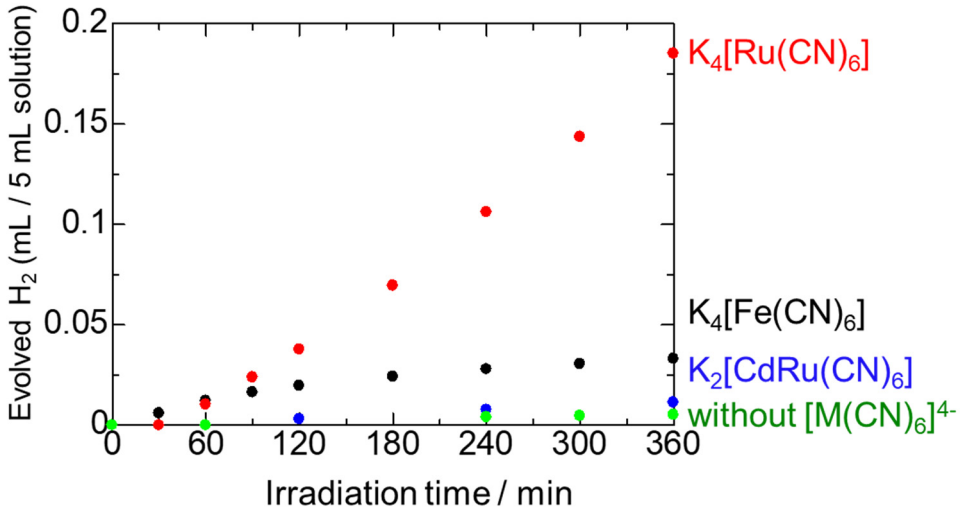

Figure S3. Photocatalytic hydrogen evolution reaction with Pt/CdS-NR (2 mg) in a 200 mM acetate buffer (pH=5.0) which contained (red) 0.01 M $K_4[Ru(CN)_6]$, (black) 0.1 M $K_4[Fe(CN)_6]$, or (blue) 0.1 M $K_2[CdRu(CN)_6]$ as electron sources under Ar atmosphere. A blue LED (λ = 470 ± 10 nm) was used as the light source. Green plots show the result in the absence of $[M(CN)_6]^{4-}$ electron source.

Table S1. Zeta potentials of the Pt/CdS-NR in the absence/presence of $K_4[M(CN)_6]$ (M = Fe, Ru) in 0.2 M acetate buffer aqueous solution.

	Zeta potential (mV)	Adsorption amount of $[M(CN)_6]^{4-}$ ($mol \cdot cm^{-2}$) [a]
Without	−11.7	-
With $K_4[Fe(CN)_6]$	−28.9	1.72×10^{-11}
With $K_4[Ru(CN)_6]$	−32.6	1.39×10^{-11}

[a] Estimated by the Guoy-Chapman-Stern (GCS) model of the double layer with the assumption that the zeta potential could be approximated as the potential at the Stern layer.[S1]

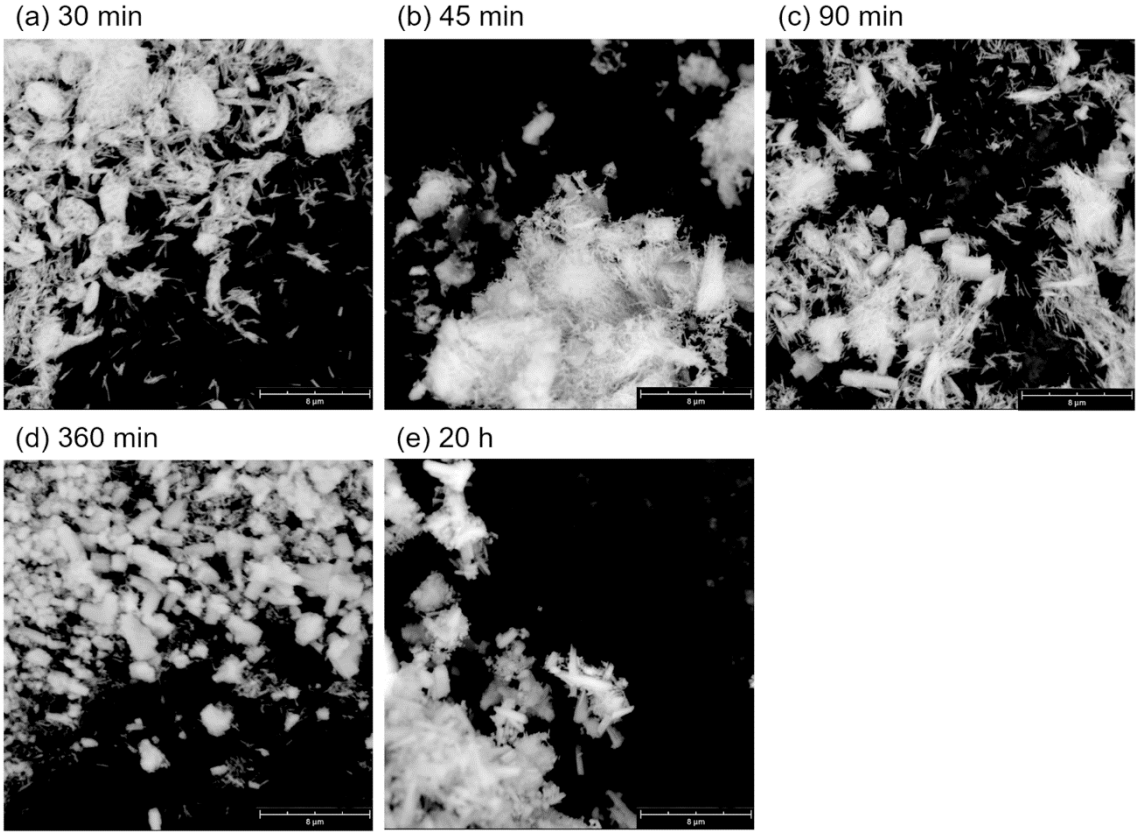

Figure S4. SEM images of the Pt/CdS-NR sample after photocatalytic H_2 evolution reaction for (a) 30, (b) 45, (c) 90, (d) 360 min, and (e) 20 h in the presence of $K_4[Ru(CN)_6]$. Scale bar in each image shows 8 μm length.

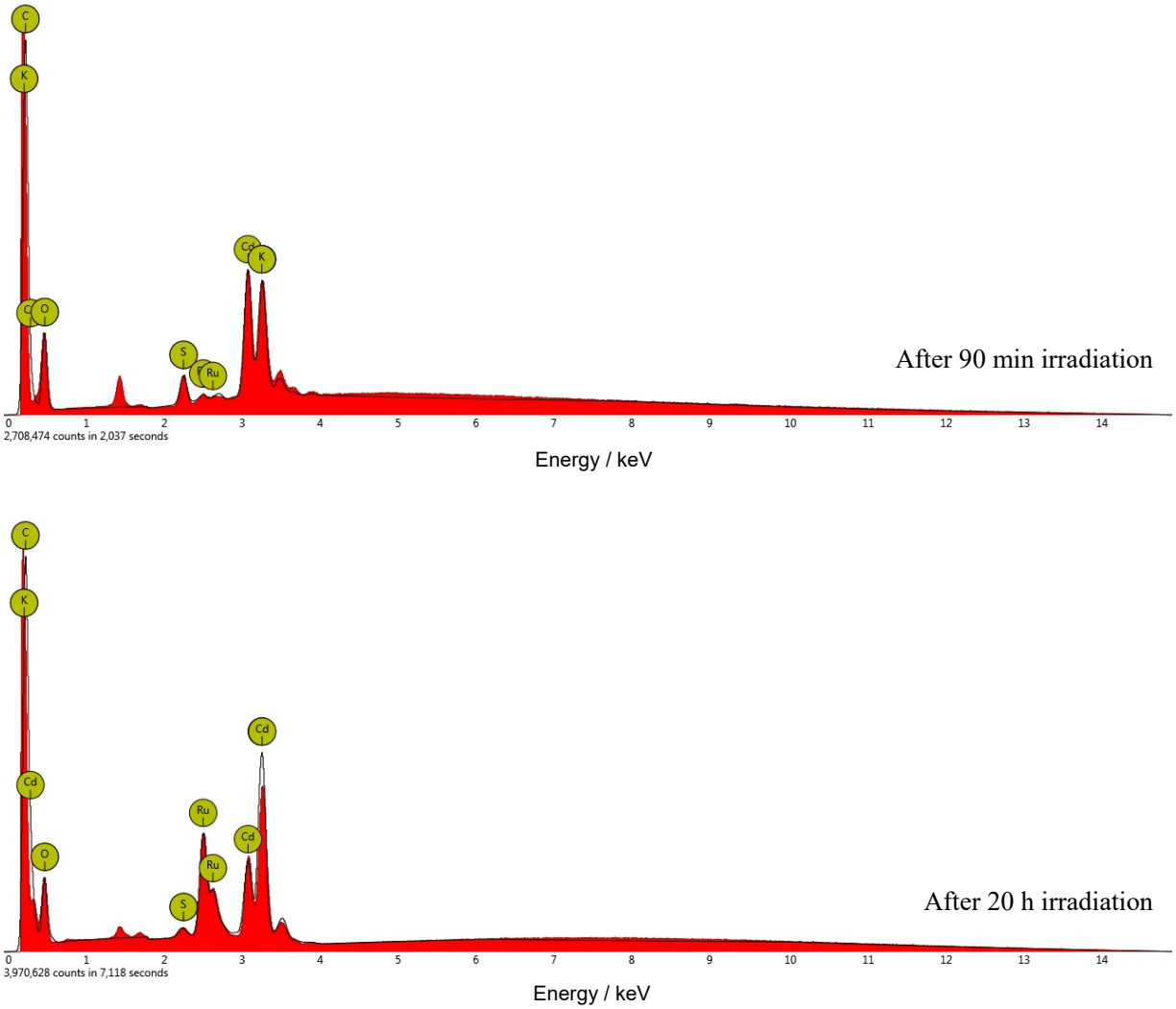

Figure S5. Energy dispersive X-ray spectra of the Pt/CdS-NR samples after photocatalytic H_2 evolution reaction for (top) 90 min and (bottom) 20 h in the presence of $K_4[Ru(CN)_6]$.

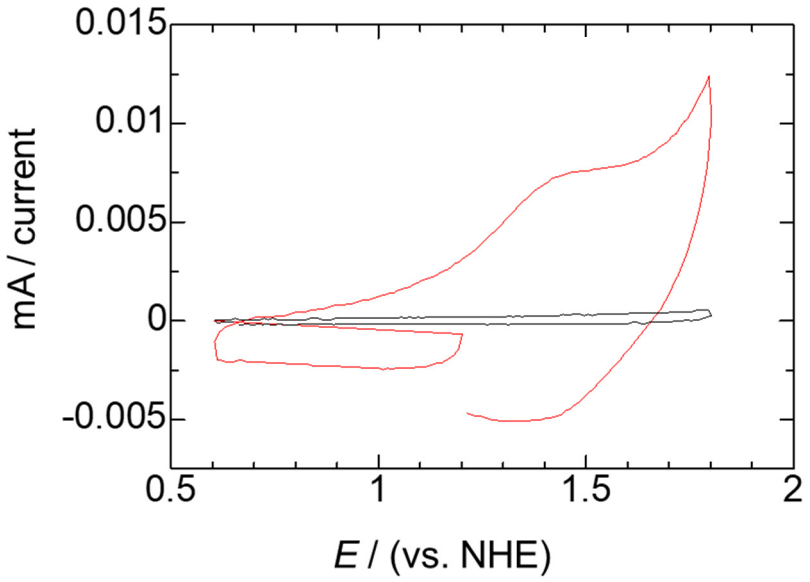

Figure S6. Cyclic voltammogram of the Prussian-white analogue $K_2Cd[Ru(CN)_6]$ modified ITO electrode. Black and red line were bare ITO electrode and $K_2Cd[Ru(CN)_6]$ modified ITO electrode. 0.1 M $TBAPF_6$ CH_3CN solution, Pt wire, and Ag/Ag^+ were used as the supporting electrolyte, counter electrode, and reference electrode, respectively. Scan rate was 50 mV/s.

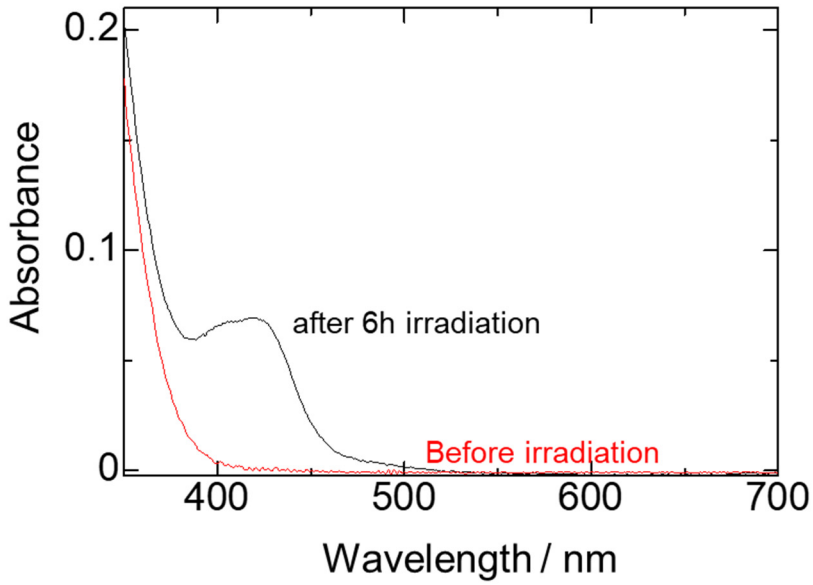

Figure S7. Change of UV-Vis absorption spectra of the reaction solution containing Pt/CdS-NR photocatalyst (2.0 mg) and 0.01 M $K_4[Fe(CN)_6]$ in 200 mM acetate buffer aqueous solution. A blue LED ($\lambda = 470 \pm 10$ nm) was used as the light source. The solution was diluted to 10 times by adding deionized water before the spectral measurement.

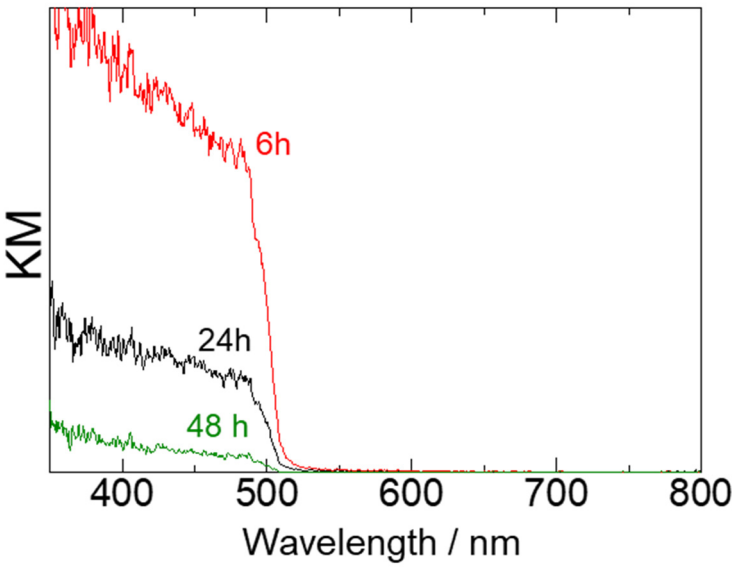

Figure S8. Change of UV-Vis diffuse reflectance spectra of the Pt/CdS-NR photocatalyst after (red) 6 h, (black) 24 h, and (green) 48 h light irradiation (λ = 470 ± 10 nm) in the presence of 0.01 M $K_4[Ru(CN)_6]$ in 200 mM acetate buffer aqueous solution. Each sample was isolated by centrifugation and washed by water for several times.

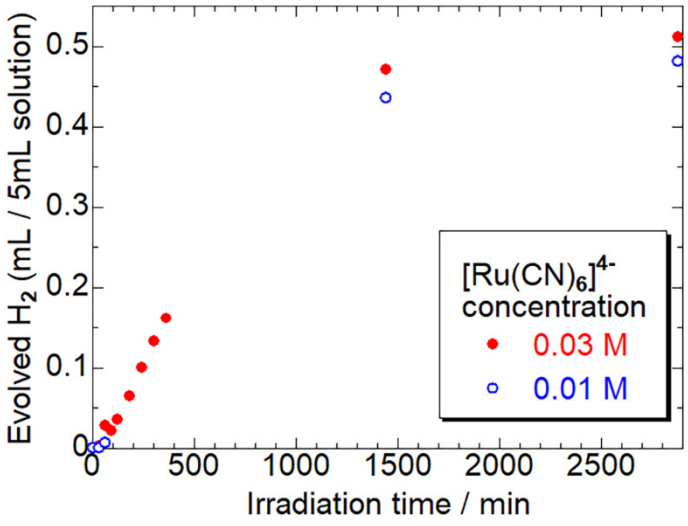

Figure S9. Photocatalytic hydrogen evolution reaction with Pt/CdS-NR (2.00 mg) in a 200 mM acetate buffer (pH=5.0) that contained (red closed circle) 0.03 M or (blue open circle) 0.01 M $K_4[Ru(CN)_6]$ as the electron source under an Ar atmosphere. A blue LED (λ = 470 ± 10 nm) was used as the light source.

Estimation of the amount of CdRu-PW produced

To estimate the amount of CdRu-PW produced, we measured the sample mass after the photocatalytic H_2 evolution reaction by centrifugation to remove all solvent and soluble reagents (e.g., acetate buffer and $K_4[Ru(CN)_6]$ redox mediator). After washing with copious amounts of deionized water, the obtained precipitate including the powdery Pt/CdS-NR photocatalyst and insoluble CdRu-PW particles was dried under vacuum for 1 day. The sample mass was then measured using an electronic balance. In this estimation, we presumed the following points:

A: The photocorrosion of CdS-NR produces the same amount of Cd^{2+} and S^{2-} ions.

B: All produced Cd^{2+} cations precipitate as insoluble CdRu-PW (= $K_2[CdRu(CN)_6]$).

C: All produced S^{2-} anions donate two electrons to the Pt/CdS-NR photocatalyst to form an equimolar amount of H_2 and are then oxidized to precipitate as insoluble S^0.

D: The mass of the Pt co-catalyst is negligibly smaller than that of CdS-NR.

On this basis, the following photochemical reaction could be expected to occur:

$$CdS + aK_4[Ru(CN)_6] + 2aH^+ \rightarrow (1-a)\,CdS + a\{K_2[CdRu(CN)_6]\} + aS + aH_2 \qquad (1)$$

where a denotes the molar ratio of photocorroded CdS-NR. Since the initial mass of Pt/CdS-NR was 2.00 mg (~13.8 μmol), the term a can be expressed by Eq. (2) using the molecular weights of CdS (Mw = 144.38), $K_2[CdRu(CN)_6]$ (Mw = 447.78), sulfur (Mw = 32.066), and the measured sample mass (shown as "*b*"):

$$144.48(13.8 - a) + 447.78a + 32.066a = b \qquad (2)$$

The first, second, and third terms on the right-hand side of Eq. (2) correspond to the masses of the remaining CdS-NR, *in situ* generated CdRu-PW, and sulfur, respectively. As mentioned in the manuscript, after 6 and 21 h of irradiation, the sample mass "*b*" was measured to be 3980 and 4500 μg, respectively. Then, the amount of CdRu-PW produced, which equals the amount of photo-corroded CdS-NR, was obtained by these values into term "*b*" of Eq. (2).

a = 5.92 μmol (6 h irradiation), 7.47 μmol (21 h irradiation)

Since the initial molar amount of CdS-NR was 13.8 μmol, ~42.8 and 54.1% of CdS-NR was estimated to be photo-corroded after 6 and 21 h of irradiation, respectively. These results are listed in Table 1 in our manuscript.

References

S1. B. J. Kirby, E. F. Hasselbrink Jr., *Electrophoresis*, 2004, **25**, 203-213.