Supplementary Information

Robust Dye-sensitized Overall Water Splitting System with Two-step Photoexcitation of Coumarin Dyes and Metal Oxide Semiconductors

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Experimental

a) Preparation of Dye-adsorbed Pt/$H_4Nb_6O_{17}$ photocatalysts

Layered niobium oxide ($K_4Nb_6O_{17}$) was prepared by the calcination of a stoichiometric mixture of K_2CO_3 and Nb_2O_5 in a platinum crucible at 1473 K for 15 min. For introducing Pt nanoparticles (0.5 wt%) as a cocatalyst into interlayer space of catalyst, $K_4Nb_6O_{17}$ powder was stirred in aqueous solution containing required amount of $\{Pt(NH_3)_4\}Cl_2$ at room temperature for 3 days, and then methanol (10 vol%) was added into the solution and irradiated by a 300 W Xe lamp for 12 h for photocatalytic reduction of $\{Pt(NH_3)_4\}^{2+}$ to metallic Pt. After washing, the sample was stirred in an aqueous HCl solution (0.5 mol L^{-1}) for 12 h to exchange K^+ ions at interlayer space into H^+. The sample was then treated with 3:1 concentrated HCl/HNO_3 at about 90 °C for 1 h in order to remove Pt particles deposited on external sites of $K_4Nb_6O_{17}$. The material thus obtained is referred to as Pt/$H_4Nb_6O_{17}$.

The Pt/$H_4Nb_6O_{17}$ powder (0.5 g) was suspended in an acetonitrile-ethanol mixed solution (1:1 v/v, 50 mL) containing the dye (0.3 mmol L^{-1}) and stirred in dark for 24 h. After separating the powder sample from the dye solution by centrifugation, it was washed once with an acetonitrile-ethanol solvent and twice by acetonitrile, and finally dried in vacuum and kept in a dark environment.

b) Preparation of IrO_2 and Pt co-loaded WO_3 photocatalyst

WO_3 powder (99.99%) was obtained from High Purity Chemical Co., Japan. Pt (0.5 wt%) was loaded onto the WO_3 by impregnation from aqueous H_2PtCl_6 solution, followed by calcination in air for 1 h at 773 K. The IrO_2 (0.5 wt%) co-catalyst was then loaded on the Pt/WO_3 sample by impregnation from aqueous Na_2IrCl_6 solution followed again by calcination.

c) Photocatalytic Reactions

Photocatalytic reactions were performed using a Pyrex glass reactor connected to a closed gas-circulation system. The photocatalyst powder (50 mg) was introduced into an aqueous potassium iodide (KI) solution (0.1 mol L^{-1}, 100 mL) in the reactor, and the suspension was stirred using a magnetic stirrer bar. The system was thoroughly degassed by several cycles of evacuation and Ar gas introduction (ca. 13 kPa). The suspension was then irradiated from the top of the reactor using a 300 W Xe lamp equipped with a UV-cut filter (Hoya L-42, $\lambda > 400$ nm). The reactor temperature was maintained at a constant temperature of 288 K during the reaction using water cooling. The evolution of H_2 gas was analyzed by an in-line gas chromatograph (TCD, molecular sieve 5 A). The amount of I_3^- ions produced was determined by the absorption spectra of the solution obtained from UV-vis spectroscopy. In the case of overall water splitting, dye-sensitized Pt/$H_4Nb_6O_{17}$ (50 mg) and IrO_2-Pt/WO_3 (100 mg) were mixed in 5 mmol L^{-1} of aqueous KI solution (100 mL), which was thoroughly degassed by several cycles of evacuation and Ar gas introduction (ca. 13 kPa), and then irradiated by visible light using a 300 W Xe lamp equipped with a UV-cut filter (Hoya L-42, $\lambda > 400$ nm).

d) Electrochemical Measurements

To examine the stability of the dye molecules in the aqueous solution, the oxidation and reduction behaviors of these dyes were analyzed by cyclic voltammetry (CV) in both aqueous and acetonitrile (AN) solutions. Since these dyes are barely soluble in an aqueous solution with a neutral pH, the CV measurements were carried out using nano-porous TiO_2 electrodes with the dyes adsorbed on them (Heimer et al., *Inorg. Chem.* **1996**, *35*, 5319-5324). Porous TiO_2 film electrodes were prepared by spreading of TiO_2 nano-particle sol (Ishihara Sangyo Co. Ltd. ST-21) on conducting glass support (F-doped SnO_2). They were then dried and calcined at 723 K for 30 min in air. The TiO_2 film was immersed in an acetonitrile-ethanol solution (50:50 v/v) of dye (0.3 mmol L-1) and kept in dark for 24 h at room temperature. The dye-adsorbed TiO_2 film was washed with acetonitrile and used immediately for the electrochemical measurements.

Electrochemical measurements were conducted with a potentiostat (Princeton Applied Research, PASTAT 2263) and a one-compartment cell consisting of a dye-adsorbed TiO_2 electrode as a working electrode, a Pt counter electrode, and a reference electrode. Ag/AgCl in saturated aqueous NaCl solution and Ag/Ag^+ in 0.01 M $AgNO_3$ acetonitrile solution were used as a reference electrode in aqueous and AN solutions, respectively. CV curves of coumarin dyes adsorbed on TiO_2 electrode were examined in a dehydrated acetonitrile or aqueous solution containing 0.1 M of $LiClO_4$ as a supporting electrolyte, with the scan rate was 100 mV s^{-1}. The solution was purged with argon gas for more than 30 min before the measurements.

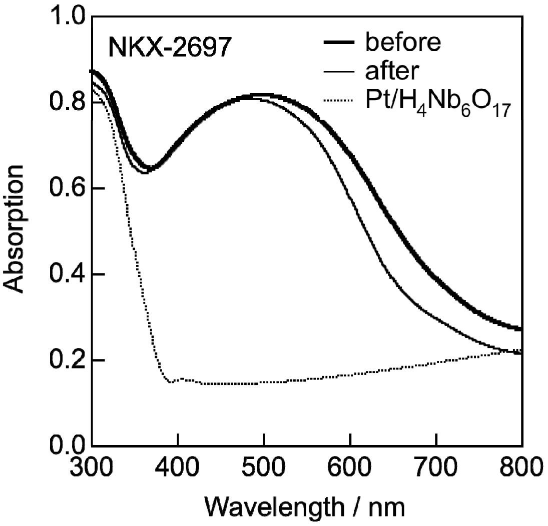

Fig. S1 Diffuse reflectance spectra of NKX-2697 adsorbed Pt/$H_4Nb_6O_{17}$ photocatalysts before and after the reaction in Fig. 2.

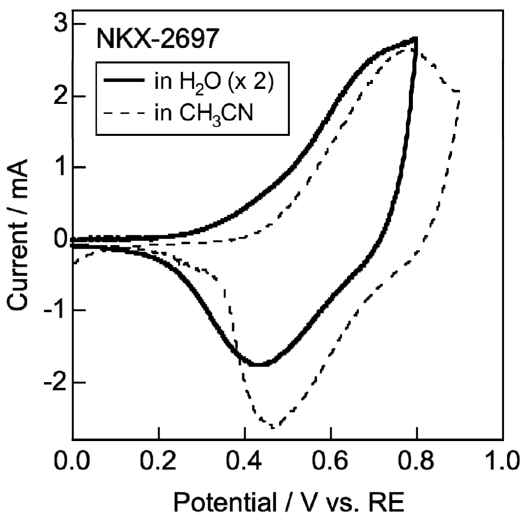

Fig. S2 CV curves of NKX-2697 absorbed on a porous TiO_2 electrode in a dehydrated acetonitrile (AN) or aqueous solution containing 0.1 M of $LiClO_4$ as a supporting electrolyte

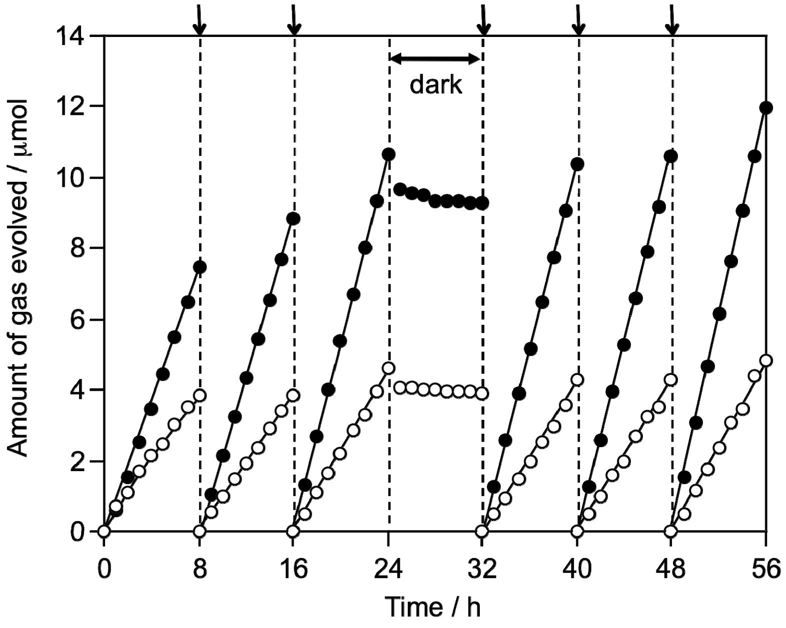

Fig. S3 Time courses of photocatalytic evolution of H_2 (closed circles) and O_2 (open circles) using a mixture of NKX-2697 adsorbed Pt/$H_4Nb_6O_{17}$ (50 mg) and IrO_2-Pt/WO_3 (100 mg) suspended in a 5 mM of KI aqueous solution under visible light ($\lambda > 400$ nm). Arrows indicate evacuation of gas phase.

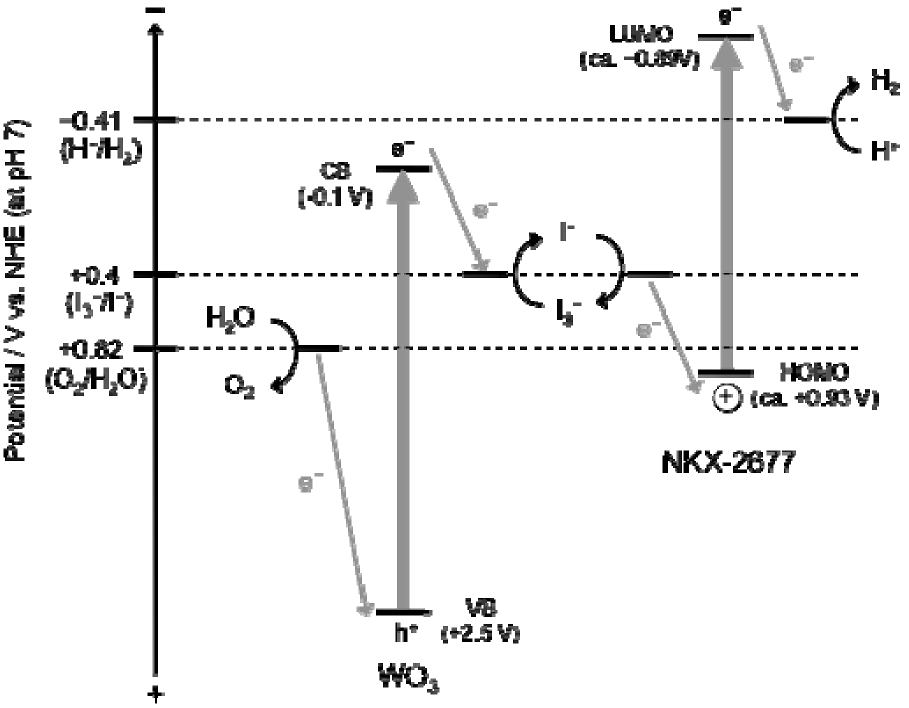

Fig. S4 Speculated reaction mechanism for overall water splitting using a mixture of NKX-2697 adsorbed $Pt/H_4Nb_6O_{17}$ and IrO_2-Pt/WO_3.