Supporting Information

Modification Effect of *meso*-Hexakis(pentafluorophenyl) [26]Hexaphyrin Aggregates on the Photocatalytic Water Splitting

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Fig. S8 Amount of H_2 and O_2 formed on RhO_X (0.1 wt%), NiO (0.1 wt%)/hexaphyrin **3** (0.5wt%)/IrO_2(0.1 wt%)–GaN:ZnO as a function of reaction time under a 300 W Xe lamp (Full arc).

Fig. S9 Photocurrent-potential characteristics of IrO_2-GaN:ZnO (blue) and hexaphyrin **3**/ IrO_2-GaN:ZnO electrodes (red) measured (scan rate, 10 mV/s) with chopped light (300 mW/cm^2 Xe lamp, 0.5 Hz).

Experimental procedures

Photocatalyst preparation.

A GaN:ZnO solid solution was prepared according to a reported method.[13] A mixture of Ga_2O_3 (Koujundo Chemical Lab. Co., Ltd., 3.0 g) and ZnO (Koujundo Chemical Lab Co., Ltd., 2.6 g) was heated under NH_3 gas flow (200 mL min^{-1}) at 1143 K for 20 h on an alumina boat. The crystal structure of the obtained powder was confirmed as a wurtzite structure by X-ray diffraction (XRD) measurements (Figure S8). The IrO_2 co-catalyst was loaded on the GaN:ZnO powder by an evaporation to dryness method with a Na_2IrCl_6•$6H_2O$ (Wako Pure Chemical Industry) aqueous solution. After calcination at 673 K for 1 h in air, IrO_2 (0.1 wt%)–GaN:ZnO was obtained. Expanded porphyrins were prepared in accordance with the literature.[12b] A solution of pentafluorobenzaldehyde (0.51 mL, 4.11 mmol) and pyrrole (0.26 mL, 4.11 mmol) in 60 mL of dichloromethane was placed in a 100 mL round-bottomed flask under nitrogen. To the solution, 30 μL of BF_3OEt_2 (0.26 mmol) was added, and the resulting mixture was stirred for 2 h. After adding DDQ, the solution was stirred for 10 h and then passed through a short alumina column. The reaction mixture was separated by silica gel column chromatography. The obtained expanded porphyrins were purified by recrystallization. The dye modification of IrO_2–GaN:ZnO was performed by an evaporation to dryness method with pyridine as the solvent. The IrO_2–GaN:ZnO powder was suspended in dye-solved pyridine (0.5 mM) and the solvent was evaporated to dryness by stirring with a glass rod at 400 K. The amounts of modification dyes were standardized as 0.5 wt% on the amount of IrO_2-GaN:ZnO in this study. Co-catalysts were loaded on the dye-modified IrO_2-GaN:ZnO by an evaporation to dryness method with an aqueous solution of Na_3RhCl_6•$12H_2O$ (Mitsuwa Chemicals) and $Ni(NO_3)_2$•$6H_2O$ (Kanto Chemical). The amounts of co-catalysts on the dye-modified GaN:ZnO photocatalyst were 0.1 wt%. Further details of the photocatalyst are described in the Supplementary Information.

Photocatalytic water splitting reaction.

Photocatalytic water splitting was performed with a closed circulating glass reactor. The catalyst (50 mg) was suspended in 30 mL of pure water, which was pre-saturated with argon gas. KOH was used to adjust the pH to 11. A quartz reaction cell including photocatalyst suspension was irradiated by a 300 W Xe lamp (Cermax PE300UV, Perkin Elmer Inc.). During the reaction, the suspension was mixed using a magnetic stir bar. Argon gas (10.67 kPa) was used as the circulating carrier gas. The amount of gases formed was measured by a gas chromatograph with a thermal conductivity detector (GC-8A, Shimadzu Corp.), which was connected to a volumetric circulating line with a vacuum pump.

UV-Vis and Fluorescence spectroscopy.

UV-vis absorption spectra were obtained by a transmission method or a reflection method using a spectrometer (U-3310, Hitachi High-Tech. Corp.) with an integrating sphere attachment. A KBr pellet was used as the reference. Fluorescence spectra were measured with a spectrophotofluorometer (F-7000, Hitachi High-Tech. Corp.).

Fluorescence lifetime measurements.

The fluorescence lifetime was measured using a lifetime spectrofluorometer (Fluorocube, Horiba Co., Ltd.) with a pulsed light emitting diode (λ = 370 nm) as the excitation light source. A band-pass filter (600 nm) was used to remove the influence of the excitation light and the fluorescence from the porphyrin dye. The powder sample was placed in a quartz cell with a screw cap. The measurements were performed at room temperature.

Cyclic voltammetry.

Cyclic voltammetry was performed using an automatic polarization system (HSV-100, Hokuto Denko Corp.) with a three-electrode configuration consisting of a Pt-wire working electrode (φ = 0.3 mm), a Pt-wire counter electrode, and a commercially available Ag/AgCl electrode as a reference electrode. Porphyrins were dissolved in CH_2Cl_2 containing 0.1 M tetrabutylammonium perchlorate (Strem Chemicals, Inc.) as a supporting electrolyte. Sample solutions were presaturated with N_2, and the measurements were performed under N_2 atmosphere. The sweep rates were 50-100 mV/s. Redox potential values were calculated as the average of the anodic and cathodic peak potentials, $(E_{pa} + E_{pc})/2$, and converted to those versus normal hydrogen electrode (NHE).

TEM observations

TEM observations and STEM-EDX analyses were performed at an acceleration voltage of 200 kV (JSM-ARM200F, JEOL Ltd.). The catalyst powder was dispersed on a Cu micro-grid (Nissin EM Corp.).

Preparation of GaN:ZnO electrodes

The GaN:ZnO film electrodes were prepared by electrophoretic method on conducting glass (FTO, Asahi Glass Co.). The electrophoretic method was performed in an aqueous solution (50 ml) containing GaN:ZnO powder (40 mg), which was dispersed by sonication for 10 minutes. Two FTO electrodes (2×3 cm) were immersed parallel in the solution with 10 mm of distance, and then 50 V of bias was applied for 3 min using a DC power supply (GPR-11H30D, Good Will Instrument Co., Ltd.). The area of GaN:ZnO film was controlled to be ca. 2×2.5 cm. The average weight of GaN:ZnO deposited on FTO was 10 mg. The IrO_2 co-catalyst was loaded on the GaN:ZnO powder by an evaporation to dryness method with a $Na_2IrCl_6 \cdot 6H_2O$ (Wako Pure Chemical Industry) aqueous solution. The electrode was dried and then calcined at 673 K for 1 h. After the IrO_2 loading, porphyrin3-solved pyridine solution (0.05 mM) was dropped on the IrO_2-GaN:ZnO/FTO electrode and then dried at 400 K to evaporate the solvent.

Photoelectrochemical measurements

The electrochemical cell used for photocurrent measurements consisted of the dye-modified GaN:ZnO electrode, a counter electrode (Pt wire), a Ag/AgCl reference electrode, and an electrolyte (0.1 M Na_2SO_4 aqueous solution). The potential of the working electrode was controlled by the potentiostat (ECstat-300, EC Frontier Inc.). Sample solutions were presaturated with N_2, and the measurements were performed under N_2 atmosphere. The electrodes were irradiated through the conducting glass by a Xe lamp (300 W, Cermax PE300UV, Perkin Elmer Inc.).

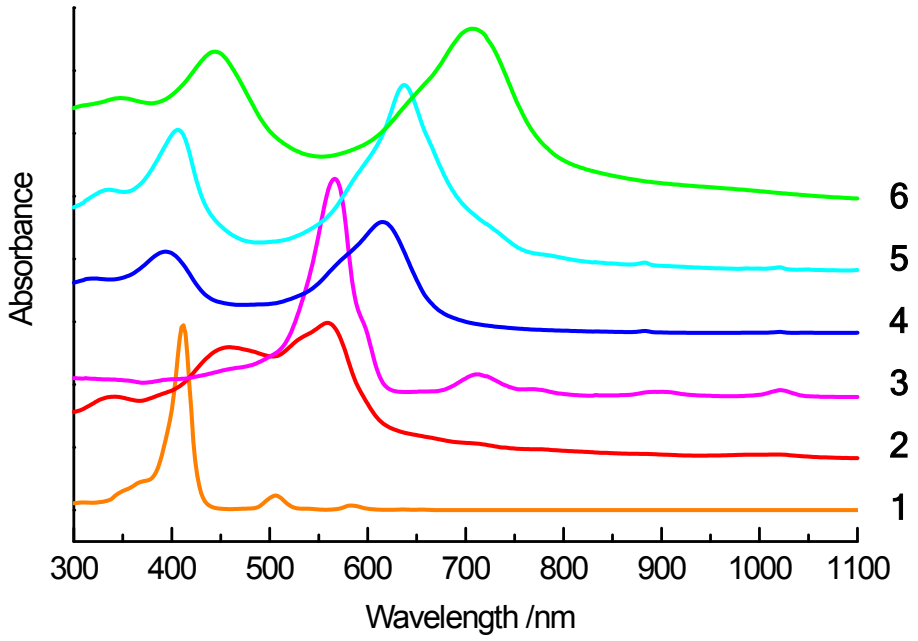

Fig. S1 UV-vis absorption spectra for compounds **1-6** in CH_2Cl_2 solvent.

Table S1 Absorption maximum wavelengths and molar absorbance coefficients for synthesized porphyrin (**1**) and expanded porphyrins (**2-6**).

Compound	λ_{max} /nm	ε_{max} /$M^{-1}cm^{-1}$
1	410	4.03×10^4
2	558	6.37×10^4
3	566	5.21×10^5
4	614	4.90×10^4
5	638	8.33×10^4
6	706	8.45×10^4

General information of the porphyrin-modified GaN:ZnO photocatalyst

The crystal structure of the GaN:ZnO powder was confirmed as a wurtzite structure by X-ray diffraction (XRD) measurements [Fig. S2(a)]. As previously reported,[1] diffraction peaks for GaN:ZnO were observed between the peaks attributed to ZnO and GaN [Fig. S2(b)]. The Ga:Zn ratio in the GaN:ZnO powder was determined by an energy dispersive X-ray spectroscopy (EDX) analyzer attached to a scanning electron microscope (VE-7800, KEYENCE Corp.) as 88:12. The specific surface area of the GaN:ZnO powder measured by using a B.E.T. surface area analyzer (BELLSORP-mini, Bell Japan Inc.) with N_2 adsorption was 2.3 m^2g^{-1}.

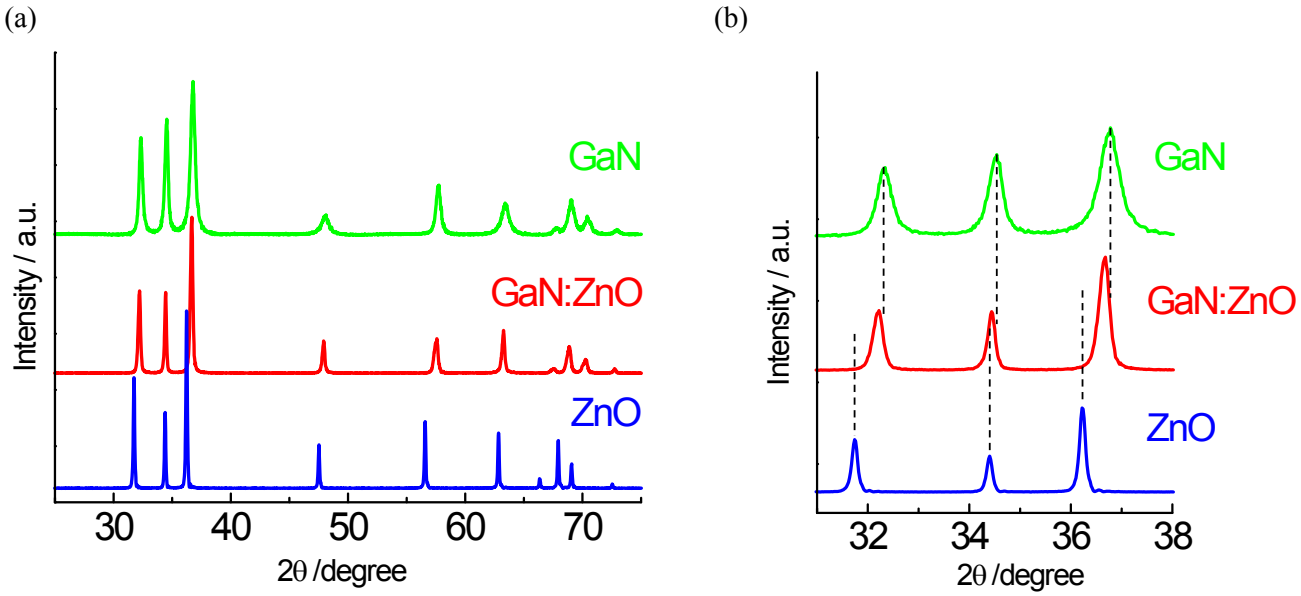

Fig. S2 XRD patterns for ZnO, GaN, and GaN:ZnO solid solutions prepared in this study (a), and expanded figure (b).

Reference

[1] K. Maeda, K. Domen, *Chem. Mater.* **2010**, *22*, 612.

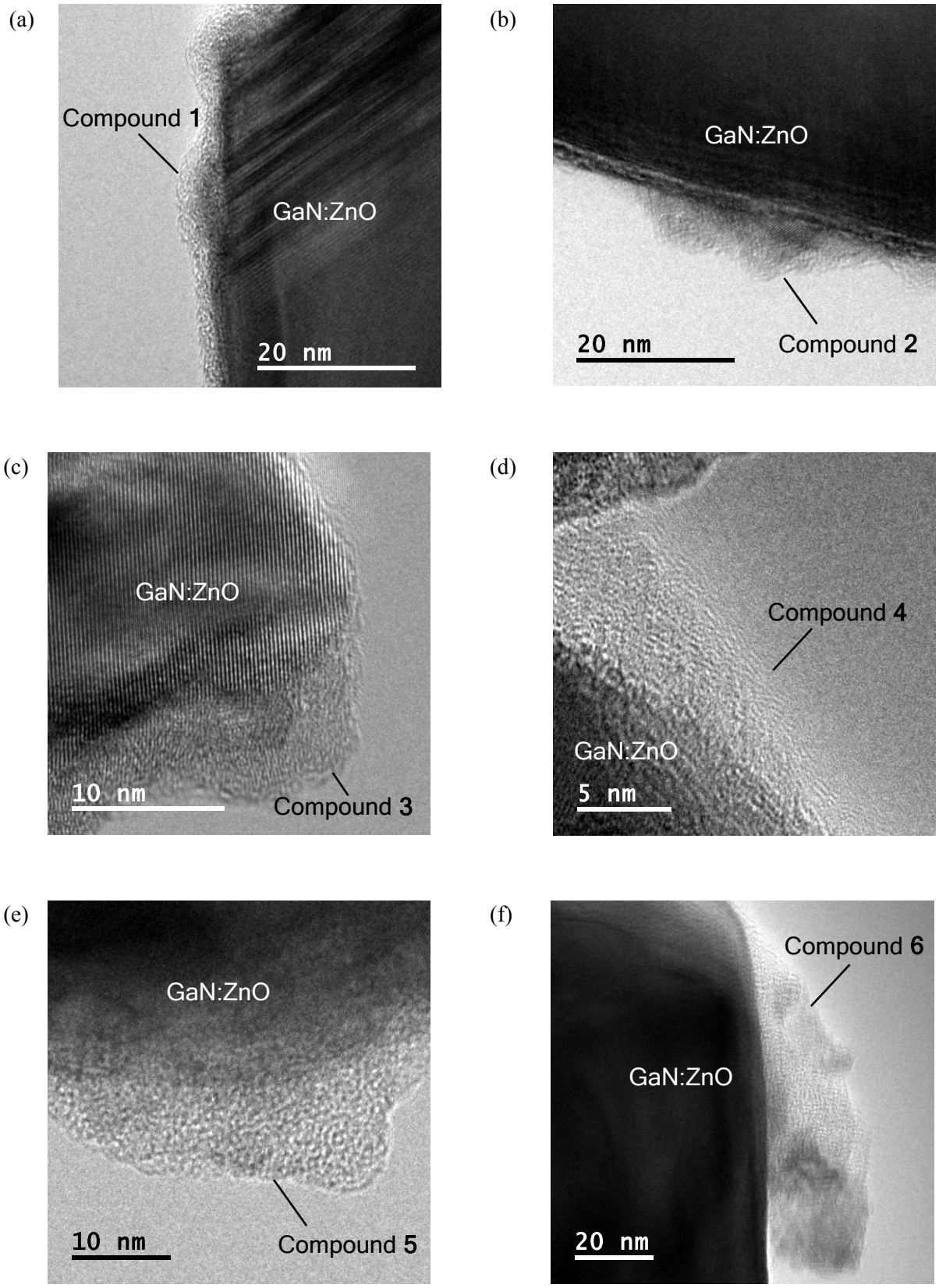

Fig. S3 TEM images of (a) meso-tetrakis(pentafulorophenyl)porphyrin (compound **1**), (b) N-fused pentaphyrin (compound **2**), (c) meso-hexakis(pentafluorophenyl) [26] hexaphyrin (compound **3**), (d) meso-heptakis(pentafluorophenyl) heptaphyrin (compound **4**) (e) meso-octakis(pentafluorophenyl) octaphyrin (compound **5**), and (f) meso-nonakis(pentafluorophenyl) nonaphyrin (compound **6**) on IrO_2-GaN:ZnO photocatalysts.

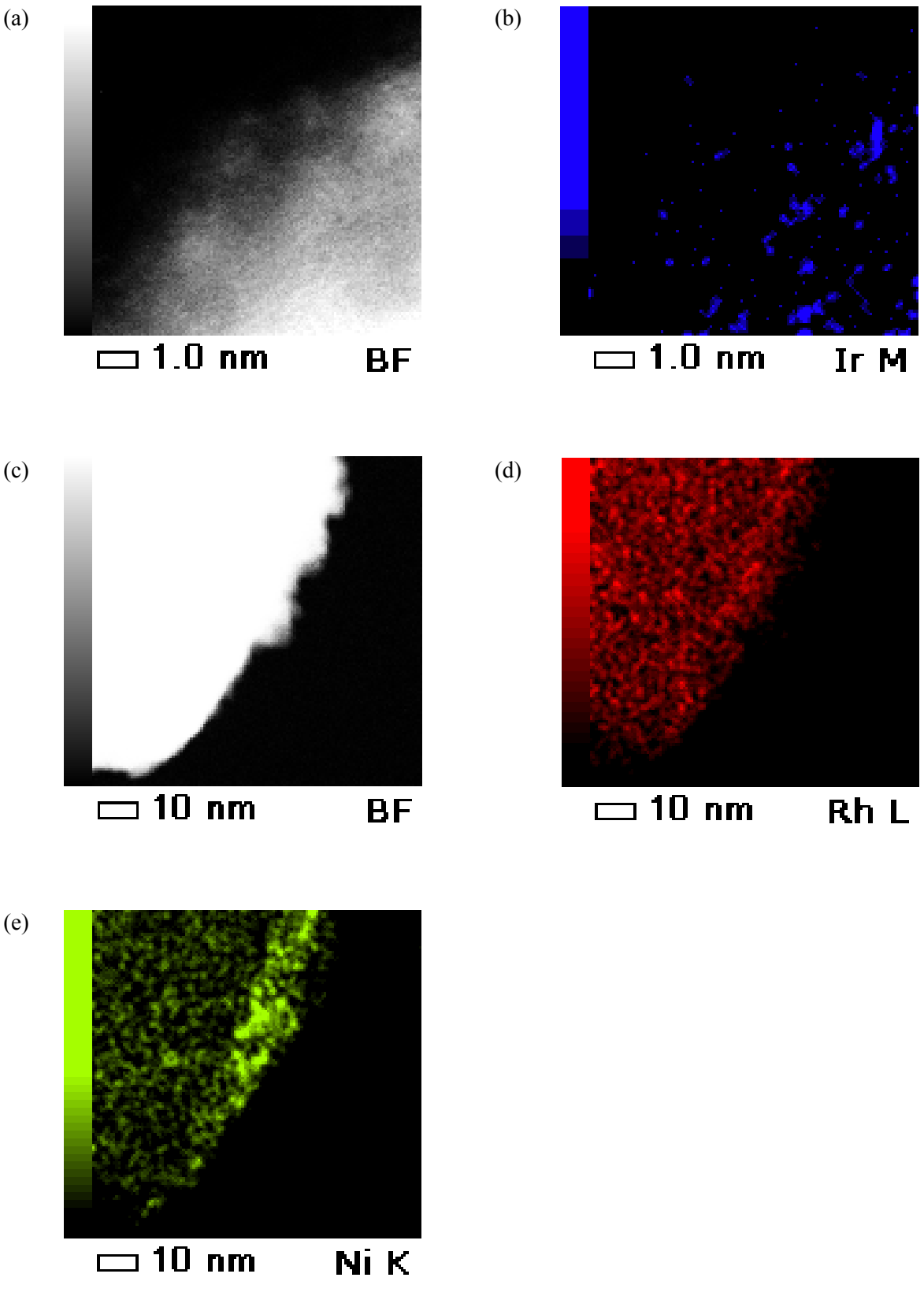

Fig. S4 HAADF-STEM images and EDX mapping of Ir M shell (a, b), Rh L shell and Ni K shell (c-e) of Rh (0.1 wt%), NiO (0.1 wt%)/hexaphyrin **3** (0.5 wt%)/IrO_2-GaN:ZnO photocatalysts.

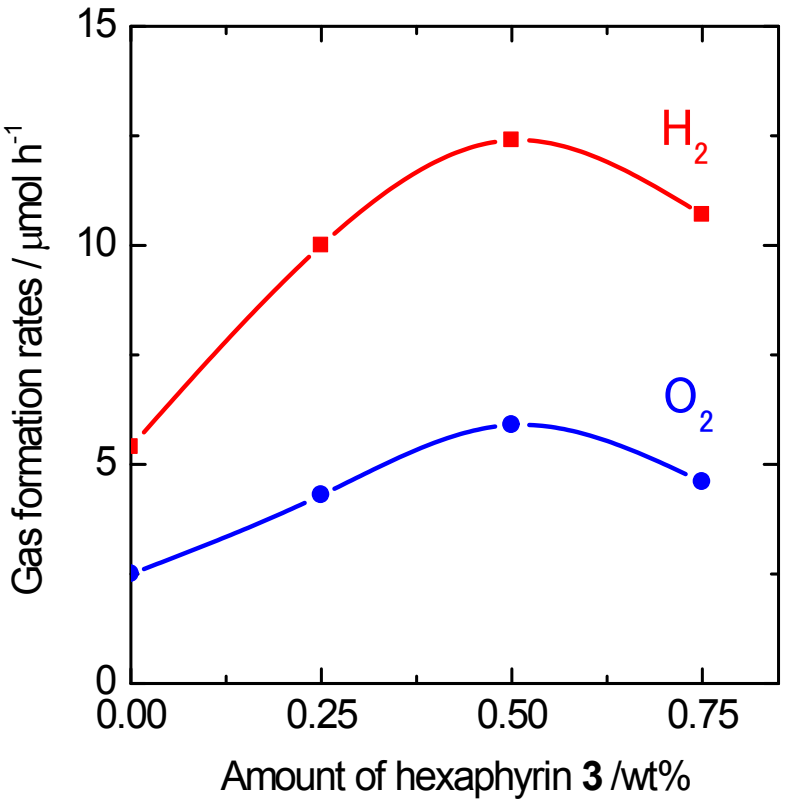

Fig. S5 Dye amount dependency of the photocatalytic activity of hexaphyrin **3** modified GaN:ZnO photocatalysts.

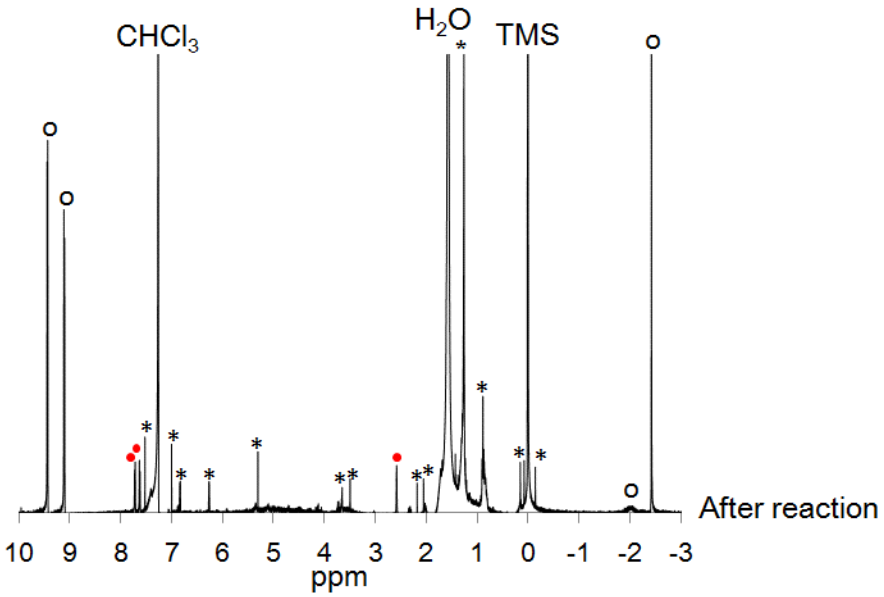

Fig. S6 ^{1}H NMR spectra of residual species of **3** after water splitting reaction. Asterisk denote impurities or spinning side band. Circle denote hexaphyrin. Closed circle denote new peaks after water splitting reaction.

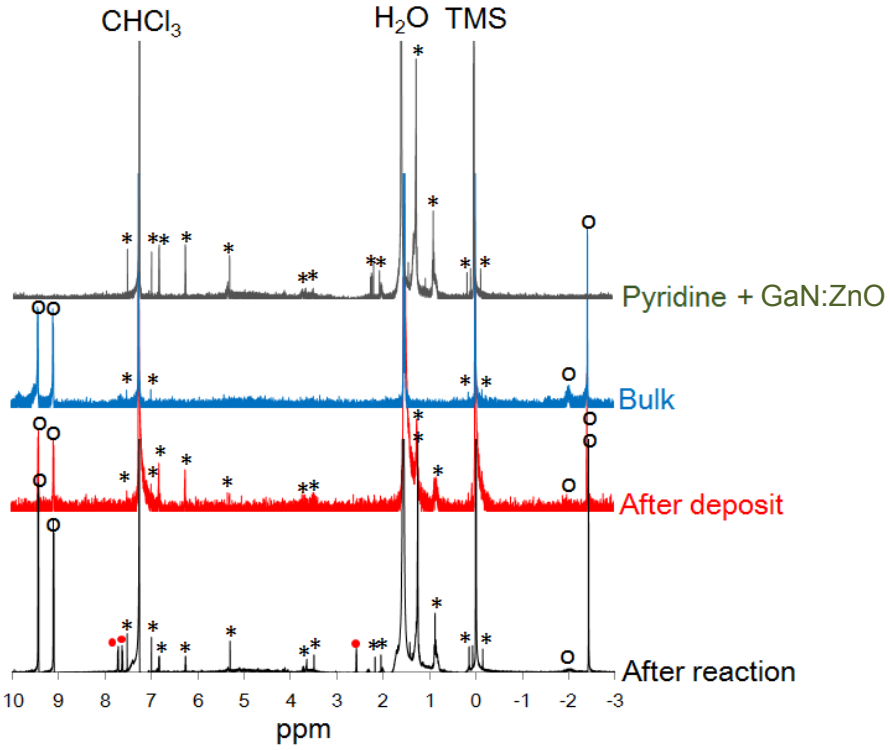

Fig. S7 ^{1}H NMR spectra of residual species of blank condition (green), bulk hexaphyrin **3** (blue), after deposit of hexaphyrin **3** by solution process (black), and after water splitting reaction (black). Asterisk denote impurities or spinning side band. Circle denote hexaphyrin peaks. Closed circle denote new peaks after water splitting reaction.

NMR measurements

The ^{1}HNMR were recorded on a Bruker AV400 (400 MHz). The ^{1}H chemical shift was reported as δ values (ppm) relative to tetramethylsilane (TMS).

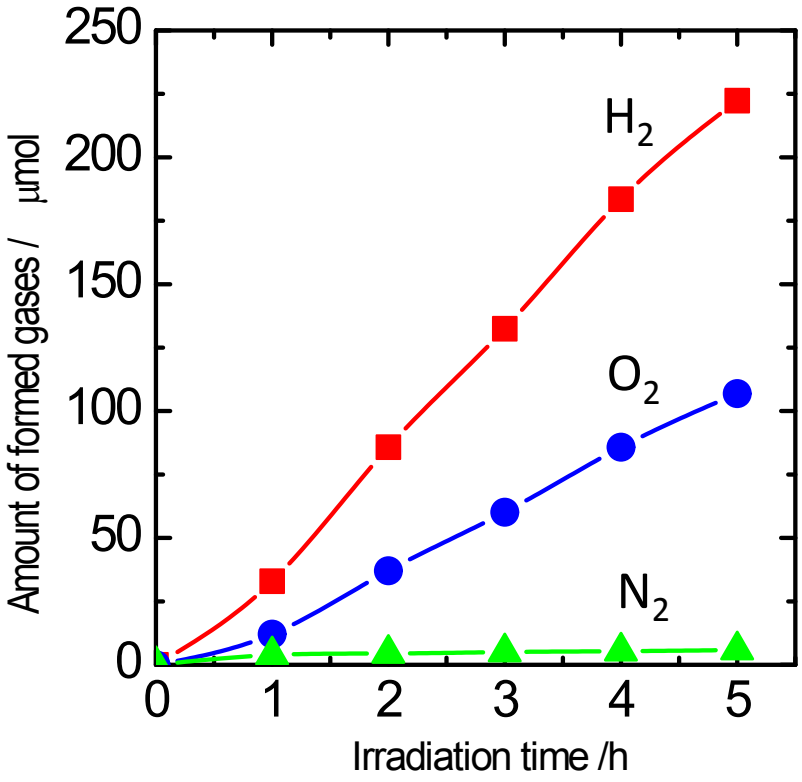

Fig. S8 Amount of H_2 and O_2 formed on RhO_X (0.1 wt%), NiO (0.1 wt%)/hexaphyrin **3** (0.5wt%)/IrO_2(0.1 wt%)–GaN:ZnO as a function of reaction time under a 300 W Xe lamp (Full arc).

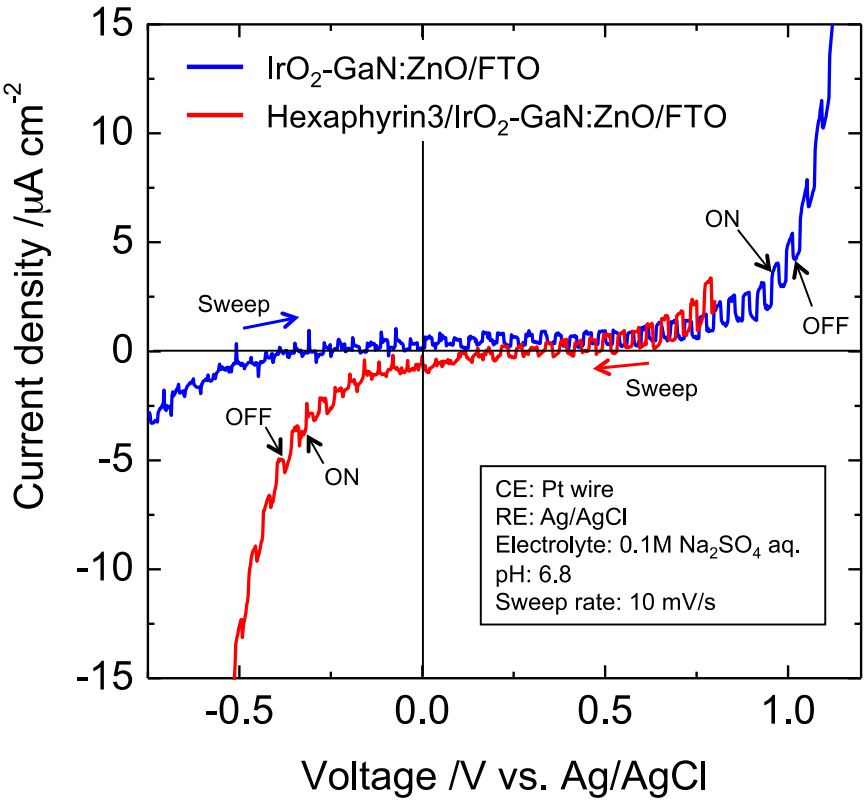

Fig. S9 Photocurrent-potential characteristics of IrO_2-GaN:ZnO (blue) and hexaphyrin **3**/ IrO_2-GaN:ZnO electrodes (red) measured (scan rate, 10 mV/s) with chopped light (300 mW/cm^2 Xe lamp, 0.5 Hz).