

Electronic supplementary information (ESI)

Metal-free hydrogen evolution with nanoparticles derived from pyrene via two-photon ionization induced by laser irradiation

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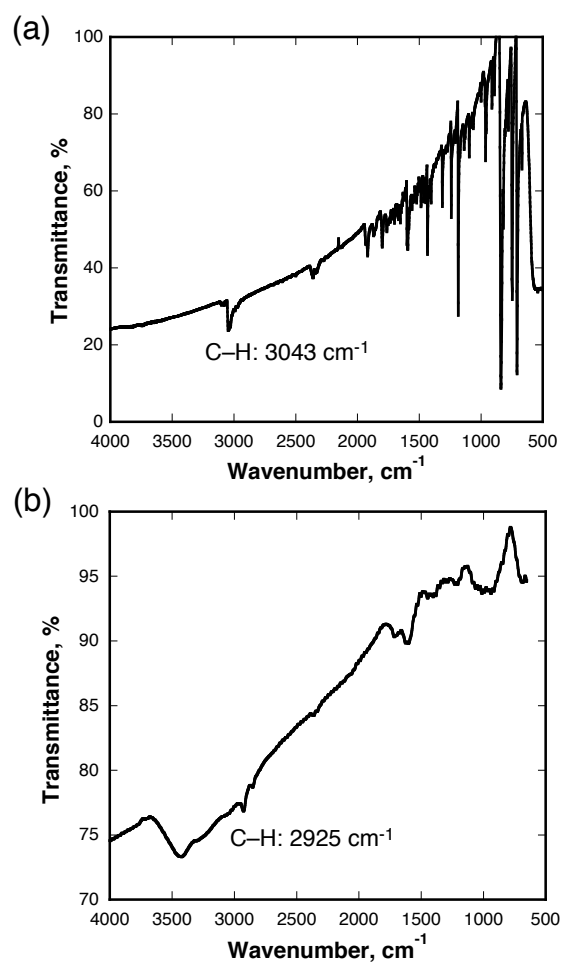


Fig. S1 IR spectra of (a) pyrene and (b) particles obtained by laser light irradiation ($\lambda = 355 \text{ nm}$; 20 mJ pulse^{-1} ; 10 pulse s^{-1}) for 4 h in deaerated cyclohexane containing pyrene ($50 \mu\text{M}$).

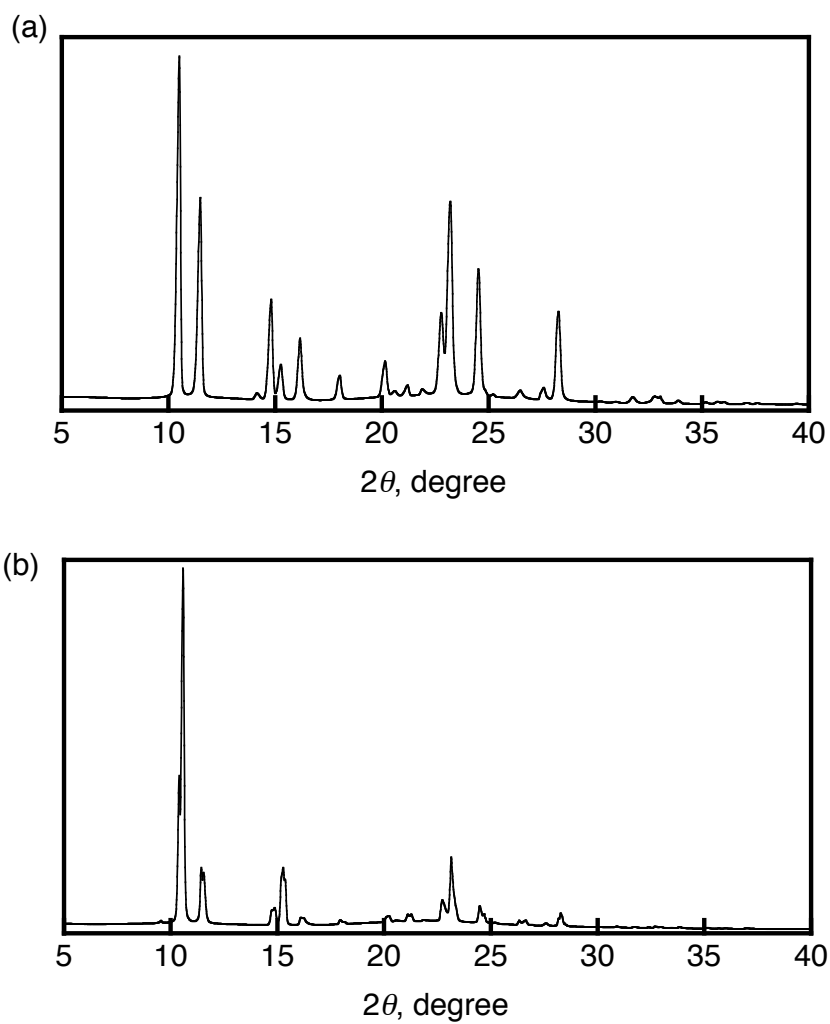


Fig. S2 PXR patterns of pyrene (a) before and (b) after laser light irradiation at 355 nm for 2 h in cyclohexane.

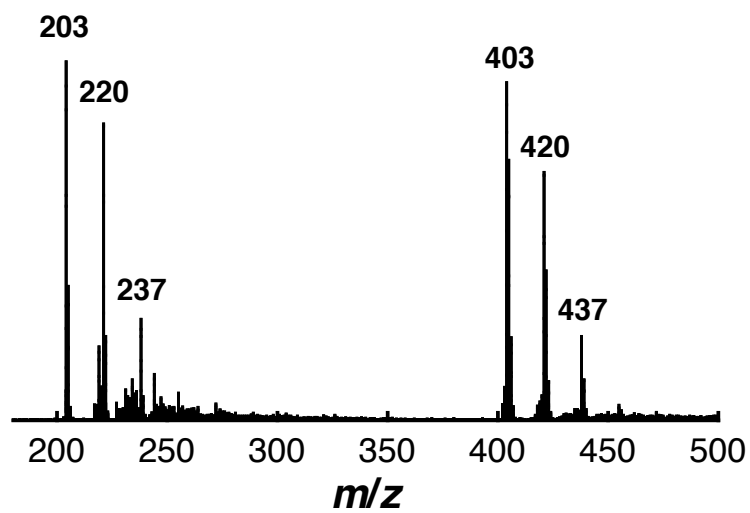


Fig. S3 MALDI-TOF-MS spectrum of reaction mixture of a cyclohexane solution (2.5 mL) containing pyrene (0.5 mM) after laser irradiation ($\lambda = 355$ nm; 20 mJ pulse⁻¹; 10 pulse s⁻¹) for 1 h. (Linear, Positive, Matrix = Dithranol).

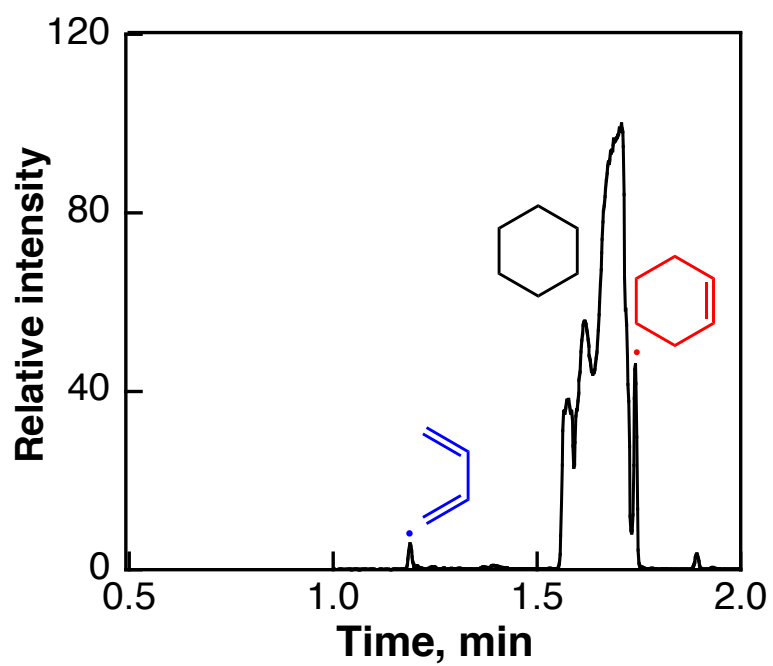


Fig. S4 GC charts of reaction mixture of a cyclohexane solution (2.5 mL) containing pyrene (50 μM) after laser light irradiation ($\lambda = 355 \text{ nm}$; 20 mJ pulse^{-1} ; 10 pulse s^{-1}) for 4 h.

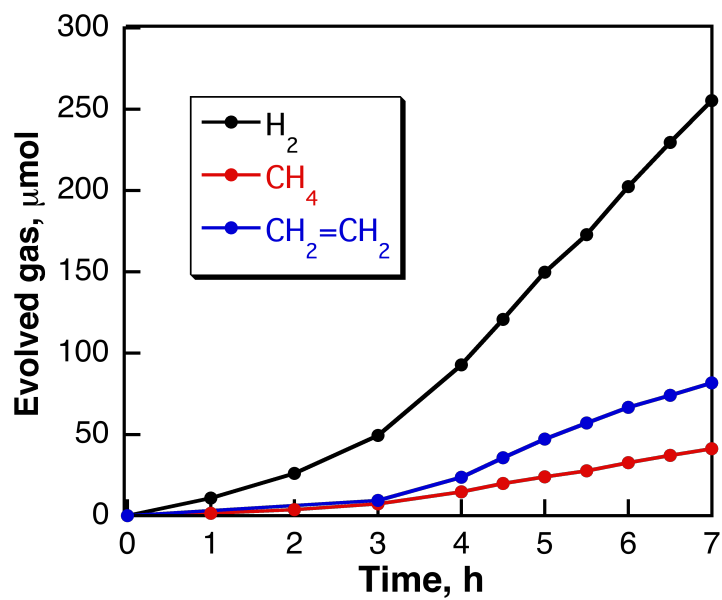


Fig. S5 Time courses of the amount of evolved H₂, methane and ethylene under laser irradiation ($\lambda = 355 \text{ nm}$; 40 mJ pulse^{-1} ; 10 pulse s^{-1}) of a cyclohexane solution (2.5 mL) containing pyrene ($50 \text{ }\mu\text{M}$).

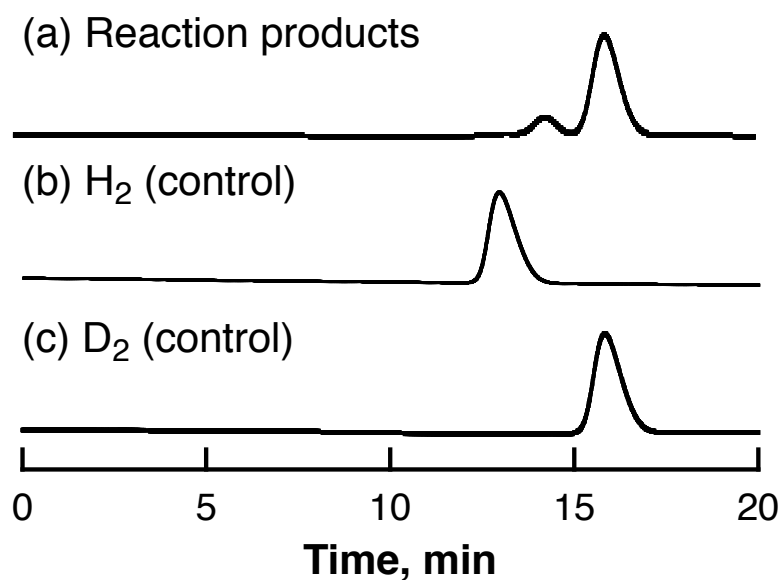


Fig. S6 GC charts of (a) evolved hydrogen after laser light irradiation ($\lambda = 355$ nm; 20 mJ pulse⁻¹; 10 pulse s⁻¹) of a cyclohexane-*d*₁₂ solution (2.5 mL) of pyrene (0.5 mM) for 4 h, (b) H₂ and (c) D₂ as control experiments. The peak at 14 min is due to HD as a coupling product of PyD[•] and PyH[•].

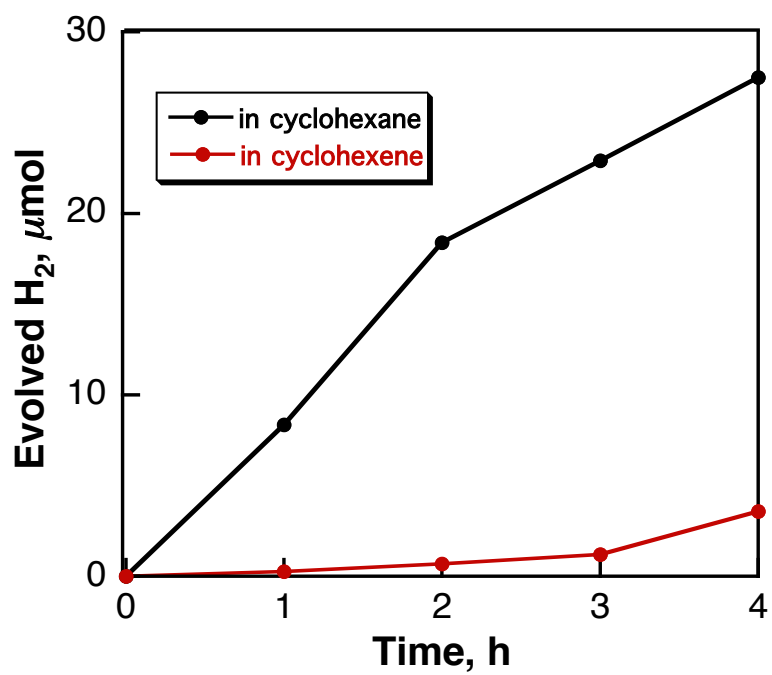


Fig. S7 Time courses of the amount of evolved hydrogen under laser light irradiation ($\lambda = 355 \text{ nm}$; 20 mJ pulse^{-1} ; 10 pulse s^{-1}) in cyclohexane and cyclohexene solutions (2.5 mL) containing pyrene (0.5 mM).

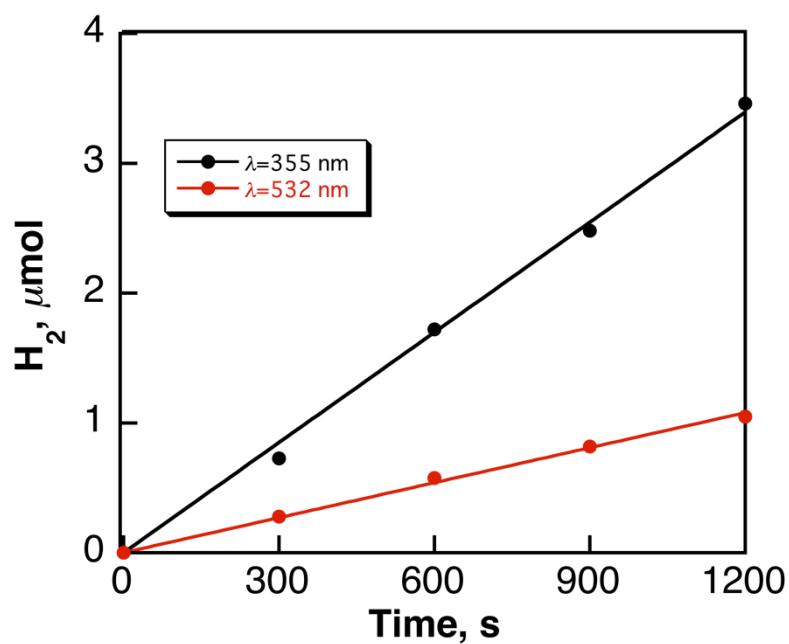


Fig. S8 Time courses of the amount of evolved H₂ under laser irradiation ($\lambda = 355$ nm and 532 nm; 20 mJ pulse⁻¹; 10 pulse s⁻¹) of a cyclohexane solution (2.5 mL) containing pyrene nanoparticles (0.4 mg).

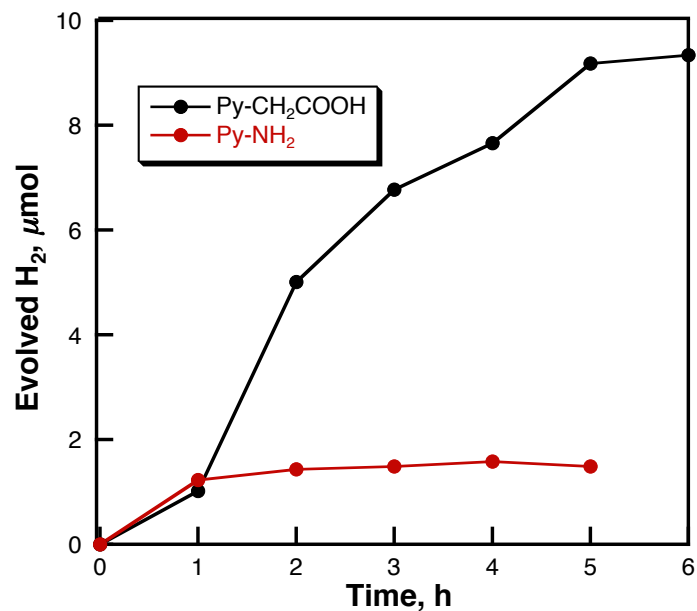


Fig. S9 Time courses of the amount of evolved H₂ under laser light irradiation ($\lambda = 355$ nm; 20 mJ pulse⁻¹; 10 pulse s⁻¹) in an aqueous solution (2.5 mL) of pyrene-1-carboxylate (0.5 mM) with NaOH (0.5 mM) (black) and 1-amino-pyrene (0.5 mM) with HCl (0.5 mM) (red).

Experimental details

Materials. Chemicals were purchased from commercial source and used without purification. Potassium ferrioxalate used as an actinometer was prepared according to the literature and purified by recrystallisation from hot water. Pyrene was obtained from Tokyo Chemical Industry, Co. Ltd (TCI). Cyclohexane and acetonitrile were of spectral grade, obtained commercially and used without further purification. Deuterated cyclohexane (C_6D_{12} , 99%) was obtained from Cambridge Isotope Laboratories, Inc., and used as received. D_2 gas (99.5%) was commercially obtained from Sumitomo Seika Chemicals Co., Ltd. Purification of water (18.2 M Ω cm) was performed with a Milli-Q system (Millipore, Direct-Q 3 UV).

Formation of particles from aromatic compounds. Cyclohexane solutions (2.5 cm³) containing pyrene (50 μ M or 0.5 mM) in a square quartz cuvette (10 mm i.d.) sealed with a rubber septum was deaerated by bubbling with nitrogen through a stainless steel needle for 5 min. The solution was then irradiated with a Nd:YAG laser (LOTIS TII, LS2134UTF) at $\lambda = 355$ nm with the power of 20 or 40 mJ pulse⁻¹ at room temperature. UV-visible spectra of the solution were measured by UV-3100PC UV-VIS-NIR scanning spectrophotometer. Size change of the particle from pyrene molecules was monitored by DLS measurements {Zetasizer Nano ZS instrument (Malvern Instruments Ltd., USA)}. MALDI-TOF-MS measurements were performed on a Kratos Compact MALDI I (Shimadzu) using dithranol as a matrix. Transmission electron microscope (TEM) images of particles were observed by a JEOL JEM 2100 operating at 200 keV. The observed samples were prepared on a copper microgrid covered with an amorphous carbon film by dropping a cyclohexane solution containing pyrene (50 μ M) after laser irradiation ($\lambda = 355$ nm, 40 mJ pulse⁻¹) for 30 min or 90 min.

Characterization of particles after laser irradiation. IR spectra measurement, EPR spectra measurement and elemental analysis were performed by using particles collected by membrane filtration (pore size: 0.1 μ m) of cyclohexane solution containing pyrene (0.5 mM) after laser irradiation ($\lambda = 355$ nm; 20 mJ pulse⁻¹). IR spectra were recorded on a JASCO FT/IR-6200, using KBr pellets. The EPR spectra were performed on a JEOL X-band EPR spectrometer (JES-ME-LX) using a quartz EPR tube containing particles at room temperature. The internal diameter of the EPR tube is 4.5 mm, which is small enough to fill the EPR cavity but large enough to obtain good signal-to-noise ratios during the EPR measurements. The amplitude of modulation was chosen to optimize the resolution and the signal-to-noise (S/N) ratio of the observed spectra. The g values were calibrated with a Mn^{2+} marker.

Hydrogen evolution from cyclohexane. C₆H₁₂ or C₆D₁₂ solutions (2.5 cm³) containing pyrene (0.5 mM) in a square quartz cuvette (10 mm i.d.) sealed with a rubber septum was deaerated by bubbling with nitrogen through a stainless steel needle for 5 min. The solution was then irradiated with a Nd:YAG laser at $\lambda = 355$ nm with the power of 20 or 40 mJ pulse⁻¹ at room temperature. The gas in the headspace was analyzed using a Shimadzu GC-14B gas chromatograph (detector, TCD; column temperature, 50 °C; column, active carbon with 60–80 mesh particle size; carrier gas, N₂) to quantify the evolved hydrogen. The reaction solution was analyzed by a Shimadzu GC-17A gas chromatograph and Shimadzu MS-QP5000 mass spectrometer to quantify produced cyclohexene. Hydrogen evolved in C₆D₁₂ after laser irradiation for 2 h was detected using a Shimadzu GC-8A gas chromatograph [detector, TCD; column temperature, 77 K (liquid N₂); column, Hydro Isopack (2.0 m, 4.0 mm i.d., GTR TEC Co., Ltd.); carrier gas, Ne] to analyze H₂, HD and D₂ gases. In the case of measuring laser intensity dependence, a cyclohexane solutions (2.5 cm³) containing pyrene particles (0.25 mg) in a square quartz cuvette (10 mm i.d.) sealed with a rubber septum was deaerated by bubbling with nitrogen through a stainless steel needle for 5 min. The solution was then irradiated with a Nd:YAG laser at $\lambda = 355$ nm with the various laser intensities (0 - 20 mJ pulse⁻¹) at room temperature. Amount of hydrogen evolved was analyzed at 600, 900 and 1200 s using a Shimadzu GC-14B gas chromatograph.

Hydrogen evolution from water. H₂O or D₂O solutions (2.5 cm³) containing 1-pyrene acetic acid (0.5 mM), NaOH (1.0 mM), and in a square quartz cuvette (10 mm i.d.) sealed with a rubber septum was deaerated by bubbling with nitrogen through a stainless steel needle for 5 min. The solution was then irradiated with a Nd:YAG laser at $\lambda = 355$ nm with the power of 20 mJ pulse⁻¹ at room temperature. The gas in the headspace was analyzed using a Shimadzu GC-14B gas chromatograph (detector, TCD; column temperature, 50 °C; column, active carbon with 60–80 mesh particle size; carrier gas, N₂) to quantify the evolved hydrogen. Amount of hydrogen evolved from H₂O solution (2.5 cm³) containing 1-aminopyrene (0.5 mM) and HCl (12 mM, 0.01 mL) was also quantified in the same way. Hydrogen evolved in a D₂O solution containing 1-pyrene acetic acid after laser irradiation for 2 h was detected using a Shimadzu GC-8A gas chromatograph [detector, TCD; column temperature, 77 K (liquid N₂); column, Hydro Isopack (2.0 m, 4.0 mm i.d., GTR TEC Co., Ltd.); carrier gas, Ne] to analyze H₂, HD and D₂ gases.

Quantum yield determinations. A standard actinometer (potassium ferrioxalate) was used for the quantum yield determination of the hydrogen evolution from cyclohexane with pyrene particles. A square quartz cuvette (10 mm i.d.) that contained a cyclohexane

solution (2.5 cm^3) of pyrene particles (0.15 mg) was irradiated with Nd:YAG laser at $\lambda = 355 \text{ nm}$ with the various laser power . Under the conditions of actinometry experiments, pyrene particles absorbed essentially 100% incident light of $\lambda = 355 \text{ nm}$. The light intensity of laser light of $\lambda = 355 \text{ nm}$ was determined as $2.3 \times 10^{-8} \text{ einstein s}^{-1}$ at $5.0 \text{ mJ pulse}^{-1}$. The photochemical reaction was monitored using a Shimadzu GC-14B gas chromatograph. The quantum yields were determined from amount of hydrogen evolved.

Powder X-ray diffraction (PXRD) measurements. PXRD patterns were recorded by a Rigaku Ultima IV. Incident X-ray radiation was produced by Cu X-ray tube, operating at 40 kV and 40 mA with Cu $K\alpha$ radiation of 1.54 \AA . A scanning rate was 4° min^{-1} from 4° to 50° in 2θ .