

SUPPORTING INFORMATION

Plasmon-Enhanced Deuteration under Visible Light Irradiation

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Supporting text

Materials.

Cadmium oxide (CdO), sulfur powder (S), L-cysteine, ethylenediamide, sodium sulfite (Na_2SO_3) and acetonitrile (CH_3CN) were purchased from Tianjing Guangfu chemical corporation. Chloroauric acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), sodium citrate, and (3-aminopropyl) triethoxysilane (APTES) were obtained from Alfa Aesar. Sodium silicate was purchased from Sigma-Aldrich. 2,2,6,6-tetramethyl-1-piperdinyloxy (TEMPO) and Dimethyl-1-pyrroline-N-oxide (DMPO) were purchased from Aldrich. All the chemicals were used without further purification.

Catalyst preparation.

Au NPs with different sizes were synthesized by reducing HAuCl_4 with NaBH_4 or sodium citrate (SC). 5 nm Au NPs were synthesized using sodium citrate as stabilizer and NaBH_4 as reducer. 16, 30 and 50 nm Au NPs were synthesized by employing different amounts of SC as reducer. Typically, 1 mL of 1.0 wt% HAuCl_4 solution was added into 96 mL water. After the solution was boiled, 3 mL, 1.5 mL or 0.7 mL of 1.0 wt% SC solution was injected into the solution to obtain Au NPs with diameters of 16, 30 or 50 nm, respectively. Au or Au@ SiO_2 NPs were centrifuged and washed with water before incubation with CdS NWs.

The photo-electrochemical analysis. The photo-electrochemical tests were performed using an electrochemical workstation (CHI 760E, Shanghai Chenhua). Clean and dry carbon fiber was employed as the working electrode. First, 5 mg catalysts were dispersed

in a mixture of 0.9 mL isopropanol and 0.1 mL nafion and then sonicated for the formation of slurry. Before deposition, the carbon fiber was tailored to leave an area of $1 \times 1 \text{ cm}^2$. And then, 100 μL slurry was deposited and dried at room temperature naturally. Electrochemical measurements were performed in a cell equipped with three electrodes, namely working electrode, reference electrode (Ag/AgCl) and counter electrode (Pt plate). Photocurrent tests were recorded at the same three electrode system. A 300 W xenon lamp with a UV-cutoff filter (400-780 nm) was employed as visible irradiation source. 0.2 M Na_2SO_3 aqueous solution served as electrolyte. EIS measurements were carried out in the same system and recorded over a frequency range of 1 Hz-100 kHz with ac amplitude of 20 mV at -0.5 V. Na_2SO_3 (0.2 M) aqueous solution was used as the supporting electrolyte. The Mott-Schottky plots were measured using the three electrode system over an alternating current (AC) frequency of 1000 Hz (electrolyte: aqueous solution of 0.2 M Na_2SO_4 , pH=6.6).

Characterization. SEM images of CdS were recorded by a JSM-7800F high-resolution scanning electron microscope. The sample was dispersed in water by ultrasonication and dropped on silicon wafer for measurement. TEM and elemental mapping images were analyzed by a Talos F200X G2, AEMC high-resolution transmission electron microscope at an accelerating voltage of 200 kV. XPS spectra were recorded on an ESCALAB 250Xi X-ray photoelectron spectroscope. The binding energy was calibrated by the C 1s peak energy at 284.6 eV. The powder X-ray diffraction (XRD) patterns were obtained on a

SmartLab 9KW X-ray diffractometer using Cu K α radiation at 25 kV and 100 mA. Extinction spectra were collected on a SPECORD 2010 plus (analytikjena) UV-vis spectrometer. Diffused reflectance spectra were acquired using a Cary 5000 UV-vis spectrometer (Viarian, USA). Raman spectra of the as-prepared catalyst were acquired using a Horiba LabRAM HR Evolution confocal Raman microscope with a 532 nm excitation laser. SERS signals of 2,6-DMPI were investigated using 633 nm laser as excitation source. It has been reported that the LO modes is sensitive to the lattice strain along the c axis. The strain associated with the lattice contractions of the c-axis was calculated by the following equation: $\Delta\omega = (1 + 3\Delta c/c)^{-\gamma} - 1$. Where $\Delta\omega$ is the LO phonon energy shift from its bulk value ω_0 (305.0 cm⁻¹) and γ is the Grueneisen parameter (1.10 for CdS).¹ Photoluminescence spectra were performed on a molecular fluorescence spectrometer (F-4600) under the excitation at 320 nm. Time-resolved PL decay curves were obtained on a FS5 fluorescence lifetime spectrophotometer (Edinburgh Instruments, UK) under the excitation at 300 nm and collection at 525 nm. Samples were suspended in CH₃CN and sonicated thoroughly before measurements. The decay curves were fitted utilizing a triexponential decay kinetic equation:

$$A(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}$$

The average PL lifetimes (τ) were calculated according to the following equation:

$$\tau = (A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2) / (A_1\tau_1 + A_2\tau_2 + A_3\tau_3)$$

Room temperature electron paramagnetic resonance (EPR) spectra were obtained over a Bruker-A300-10/12 EPR spectrometer. A Xe lamp was used as light source. In a typical

experiment, 3 mg Au/CdS was firstly dispersed in a 5 mL mixture of CH₃CN and H₂O (v:v=1:1); a desired amount of substance were then added in. The concentrations of TEMPO/DMPO, 4-iodoanisole, and Na₂SO₃ for specific experiments were fixed at 10 mM, 5 mM and 0.1 M, respectively.

Photocatalytic hydrogen evolution. Experiments in photocatalytic water splitting were performed in a top-irradiation Pyrex flask. A 300 W Xe lamp (PLS-SXE300, Beijing Trusttech Co., Ltd.) was used as the irradiation light source. Typically, 20 mg 16 nm Au/CdS photocatalysts were suspended in a 120 mL aqueous solution of 0.2 M Na₂SO₃ under magnetic stirring. Prior to irradiation, the reaction mixture was deaerated with Ar gas for 30 min to thoroughly remove the dissolved oxygen. A cooling-water jacket was employed to keep the reaction temperature at 25 °C. To evaluate the photocatalytic hydrogen production, the gas-phase composition of the photocatalytic reactor was analyzed every one hour by automatically extracting 0.5 mL gas into a GC-14C gas chromatograph equipped with a column of 5 Å molecular sieves (carrying gas: Ar). The H₂ peak was calibrated by the injection of pure H₂ to obtain the working curve.

Synthesis of 2-iodo-1-(4-iodophenyl)ethanone. 2-iodo-1-(4-iodophenyl)ethanone was synthesized according to a reported procedure.² Fine powders of CuO (0.4 g, 5.0 mmol) and I₂ (1.27 g, 5.0 mmol) were added into a solution of 1-(4-iodophenyl)ethanone (1.23 g, 5.0 mmol) in anhydrous MeOH (15 mL). The mixture was refluxed for 4 h. After the

disappearance of 1-(4-iodophenyl)ethanone (monitored by TLC), the mixture was cooled down to room temperature and filtered. The solvent was removed under reduced pressure and the residue was poured into 10% Na₂S₂O₃ solution (50 mL) to remove the excess iodine. Then the mixture was extracted with ethyl acetate (25 mL×3), and the organic layer was dried over anhydrous MgSO₄. The desired product was obtained after the removal of the solvent without further purification. M=1.8 g, yield=86%, yellow solid, ¹H NMR (400 MHz, CDCl₃): =7.84 (d, 2H), 7.63 (d, 2H), 4.31 (s, 2H); ¹³C NMR (400 MHz, CDCl₃): =191.1, 137.2, 129.3, 101.0.

Synthesis of (iodoethynyl)benzene. (Iodoethynyl)benzene was synthesized according to a reported procedure.³ N-iodosuccinimide (0.77 g, 3.42 mmol) and silver nitrate (0.12 g, 6.84 mmol) were added successively into a solution of ethynylbenzene (0.35 g, 3.42 mmol) in 20 mL acetone. The reaction mixture was stirred at 0 °C for 10 h. Then, the mixture was filtered and the organic solution was extracted with ethyl acetate (25×3 mL). The organic layers were combined and successively washed with sodium thiosulfate (1×25 mL) and brine (1×25 mL). The organic phase was then dried over anhydrous MgSO₄ and evaporated under reduced pressure to yield the product with trace of succinimide. (Iodoethynyl)benzene was purified by chromatography using petrol ether as eluting agent. M=0.59 g, yield=76%, yellow oil. ¹H NMR (400 MHz, CDCl₃): □=7.29 (m, 2H), 7.30 (m, 2H), 7.41 (m, 1H); ¹³C NMR (400 MHz, CDCl₃): □=132.4, 128.8, 128.3, 123.4, 94.2, 6.1.

Supporting Figures

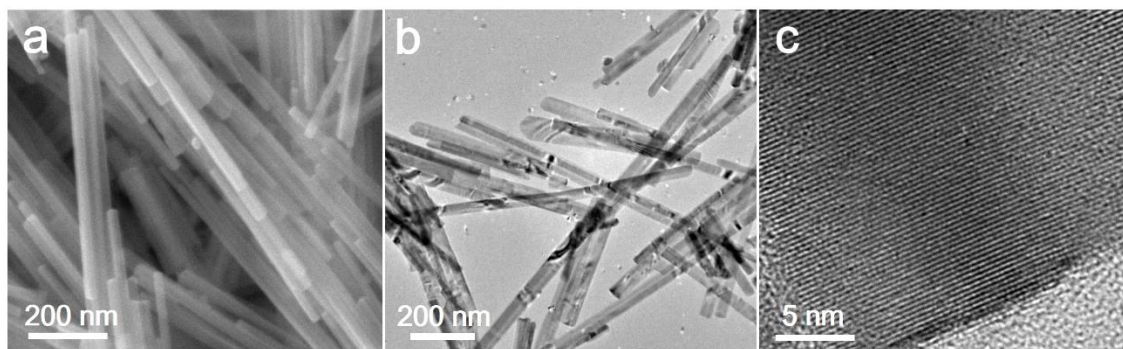


Figure S1. (a) FESEM image of CdS NWs. (b) TEM image of CdS. (c) HRTEM image of CdS.

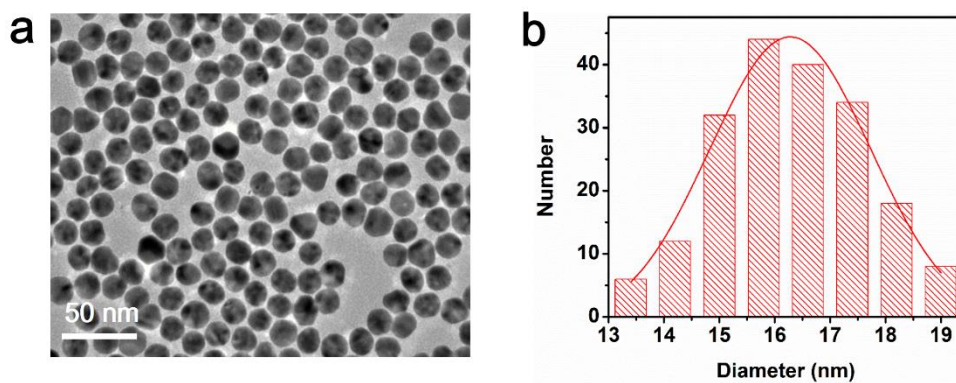


Figure S2. (a) TEM image of Au NPs. (b) Diameter distribution of Au NPs evaluated from Figure S2a.

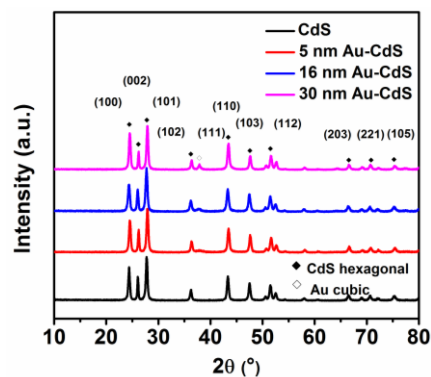


Figure. S3. XRD patterns of CdS NWs and Au/CdS.

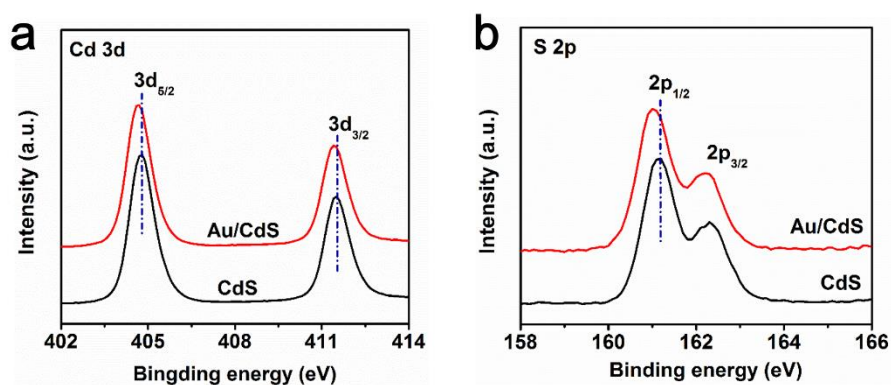


Figure. S4. XPS analysis of CdS and the Au/CdS: (a) Cd 3d, and (b) S 2p regions.

Compared with CdS, the binding energy of Cd 3d and S 2p of Au/CdS are negatively shifted by about 0.1 eV, which are attributed to the increase of electronic density in CdS after the loading of Au NPs.

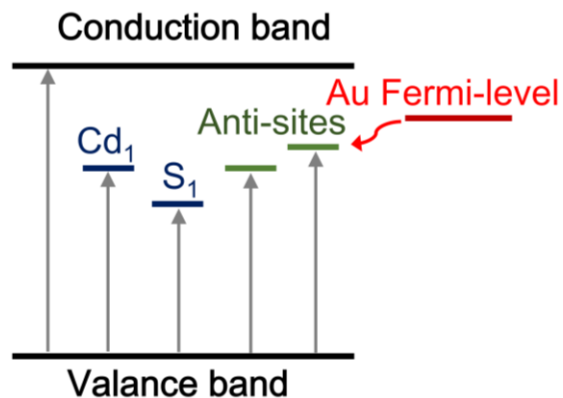


Figure S5. Transitions of the emssion levels of CdS NWs and Au/CdS.

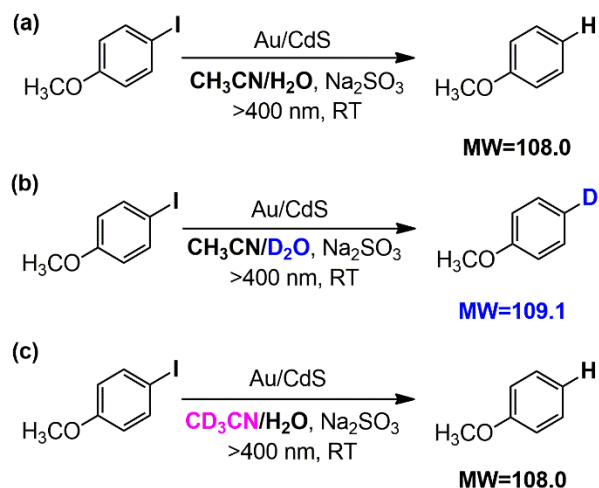


Figure S6. Determination of hydrogen/deuterium source by the dehalogenative deuteration of substrate 4-iodoanisole. The change of molecule weight from 108.0 to 109.1 when D₂O is involved confirms the hydrogen donor is water. The molecule weight does not change in the control experiment using deuterated acetonitrile.

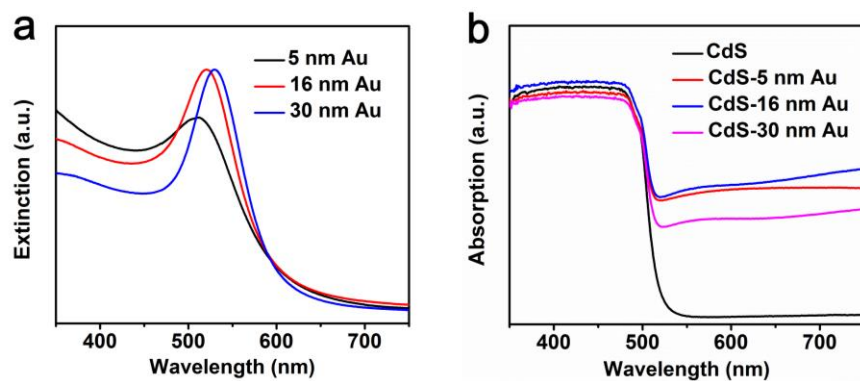


Figure S7. (a) UV-vis extinction spectra of Au NPs with different sizes. (b) UV-vis DRS spectra of CdS NWs and Au/CdS.

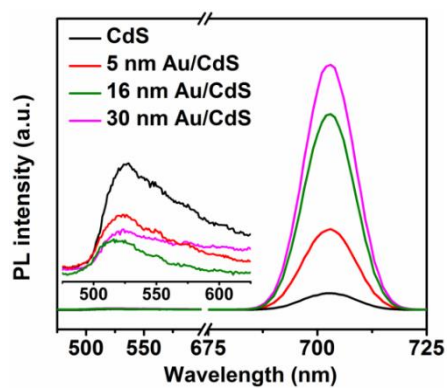


Figure S8. Steady state PL spectra of Au/CdS with different sized Au NPs.

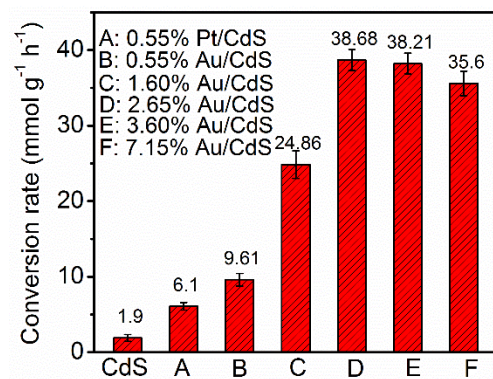


Figure S9. The conversion rates of HDI over Au/CdS catalysts with different weight percentage of Au NPs (16 nm).

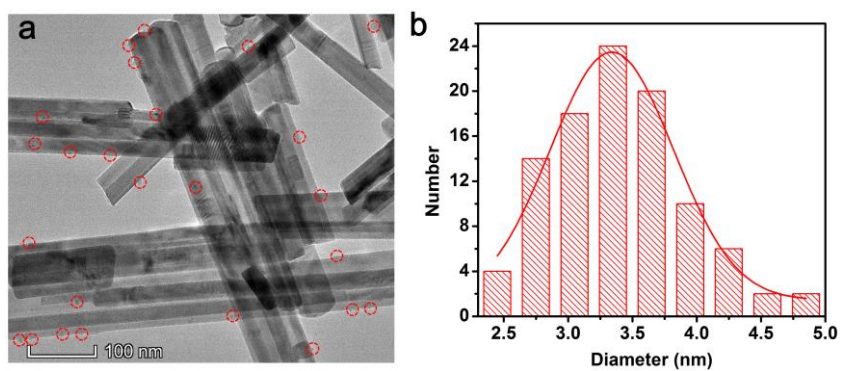


Figure S10. (a) TEM image of Pt/CdS and (b) size distribution of Pt NPs.

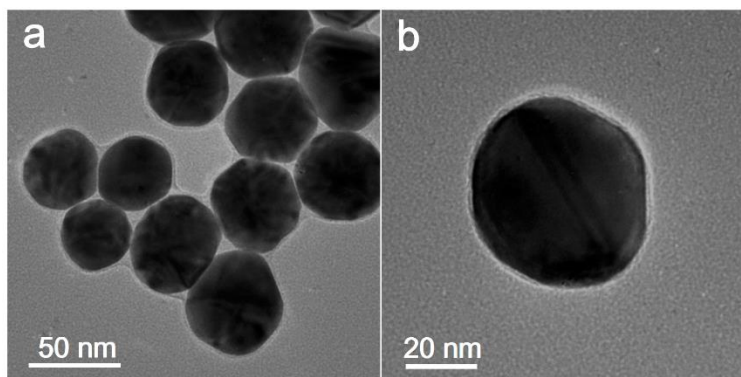


Figure S11. TEM images of Au@SiO₂. The thickness of the silica shell is determined to be ~2 nm.

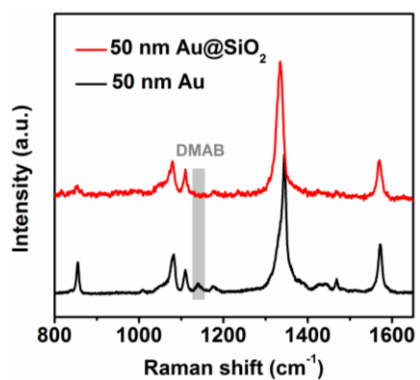


Figure S12. SERS spectra of 4-NTP under 633 nm laser excitation enhanced by 50 nm Au and 50 nm Au@SiO₂ NPs.

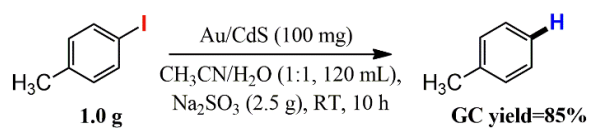


Figure S13. Scale up synthesis of toluene (2b) by the photocatalytic hydrodehalogenation.

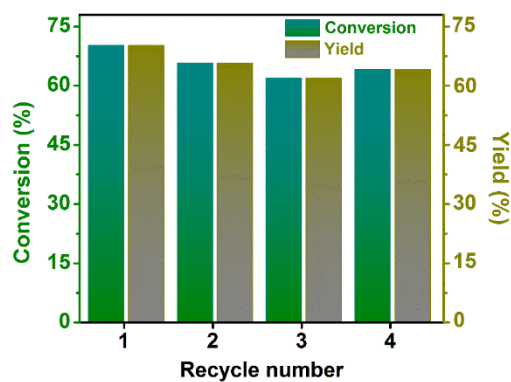
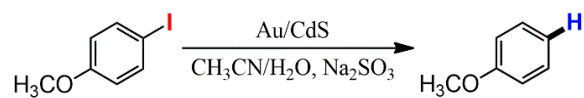


Figure S14. The photocatalytic stability of the Au/CdS at medium conversion of 4-iodoanisole. Each cycle was conducted with 0.1 mmol 4-iodoanisole under the optimized conditions.

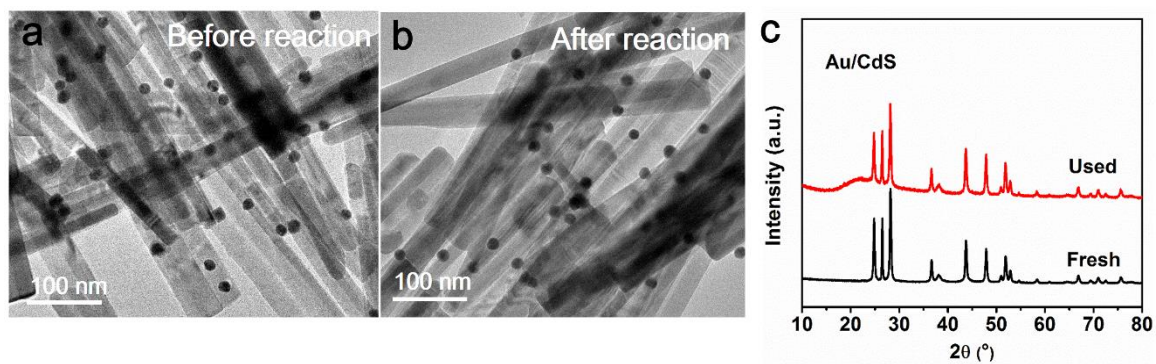


Figure S15. TEM images of Au/CdS before (a) and after reaction (b). (c) XRD patterns of Au/CdS before and after reaction.

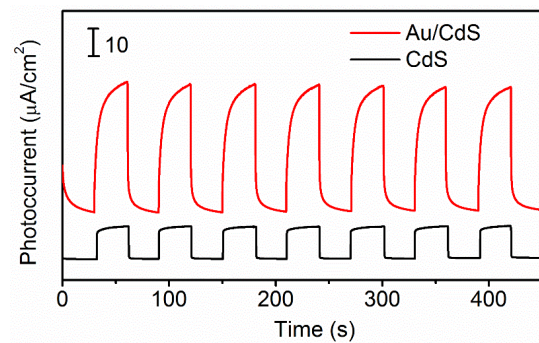


Figure S16. Photocurrent responses of Au/CdS and CdS with the visible light irradiation switched on and off.

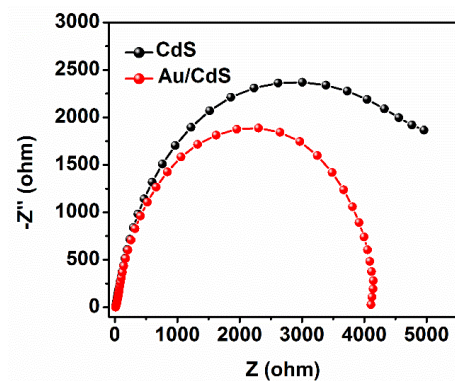


Figure S17. Electrochemical impedance spectra of Au/CdS and CdS.

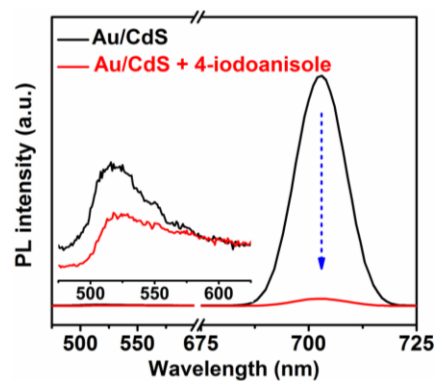


Figure S18. Room temperature PL spectra of Au/CdS with and without the addition of 4-iodoanisole.

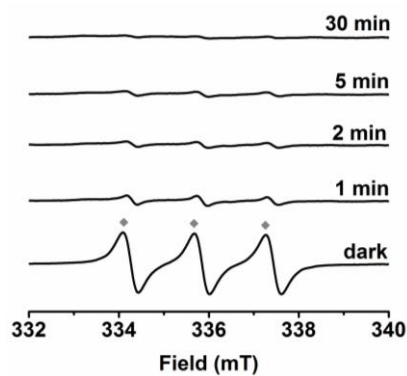


Figure S19. Quenching of TEMPO radicals in HDI. The three peaks labeled in the figure are originated from the TEMPO radical.

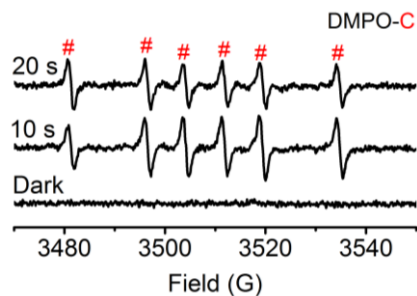


Figure S20. EPR tests of Au/CdS with DMPO, 4-iodoanisole in H₂O/CH₃CN under visible light irradiation, # represents the peaks of DMPO-C.

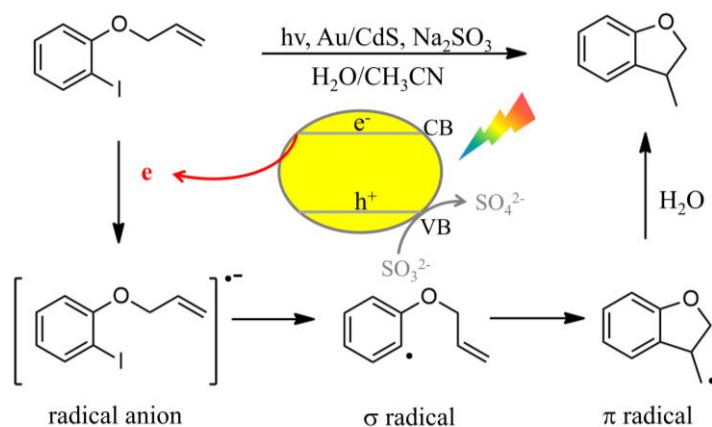


Figure S21. The established mechanism of the radical addition cyclization reaction.

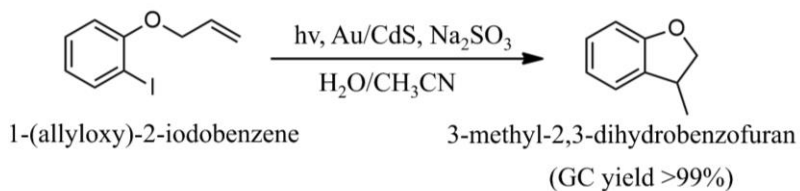


Figure S22. The radical addition cyclization reaction of 1-(allyloxy)-2-iodobenzene.

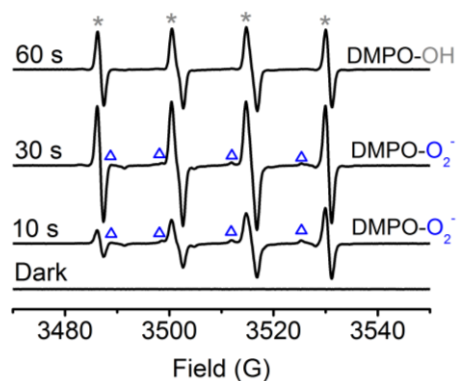


Figure S23. EPR tests of Au/CdS with DMPO in H₂O/CH₃CN under visible light irradiation without the addition of reactant molecules, * and Δ represent the peaks of DMPO-OH and DMPO-O₂⁻, respectively. H radicals were not observed, suggesting their quite active nature and short life time.

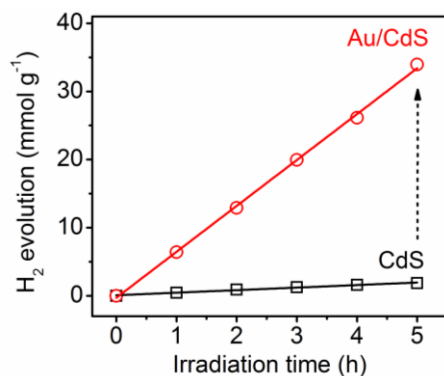


Figure S24. Photocatalytic hydrogen evolution using Au/CdS and CdS. The hydrogen evolution rate using Au/CdS was calculated to be 6.5 mmol g⁻¹ h⁻¹.

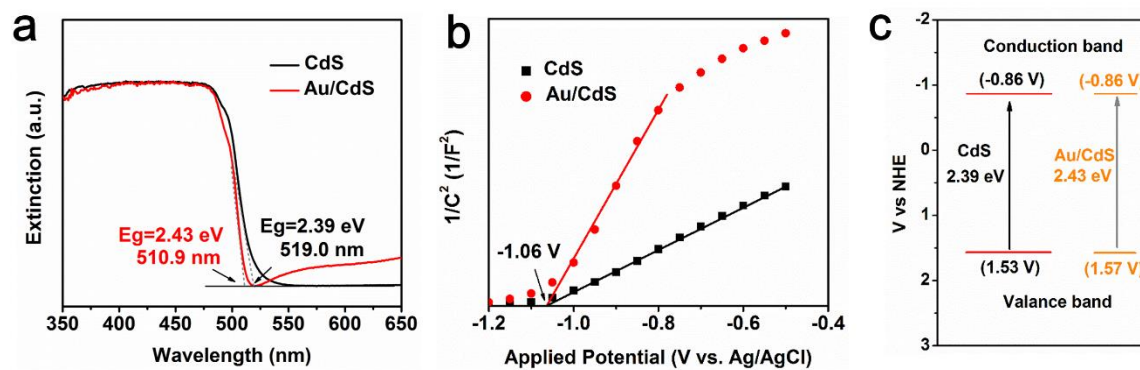


Figure S25. (a) Band gaps of CdS and Au/CdS. (b) Mott-Schottky spots of CdS and Au/CdS. (c) Energy band positions of CdS and Au/CdS.

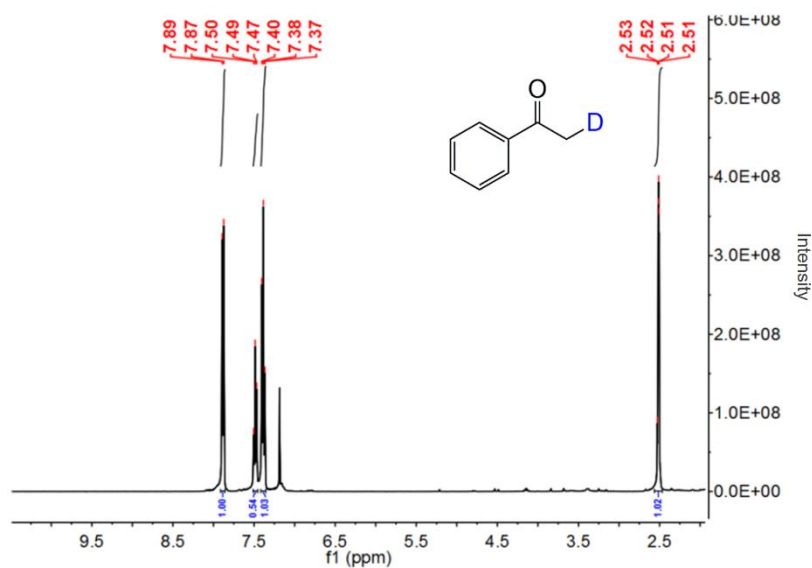


Figure S26. ^1H NMR of product 2k. Deuterated ratio=96%, ^1H NMR (400 MHz, CDCl_3): $\delta = 7.89\text{--}7.87$ (m, 2H), $7.50\text{--}7.47$ (m, 1H), $7.40\text{--}7.37$ (m, 2H), $2.53\text{--}2.51$ (m, 2.04H); HRMS (EI) 121.0634, theoretical value for $\text{C}_8\text{H}_7\text{DO}$ 121.0638.

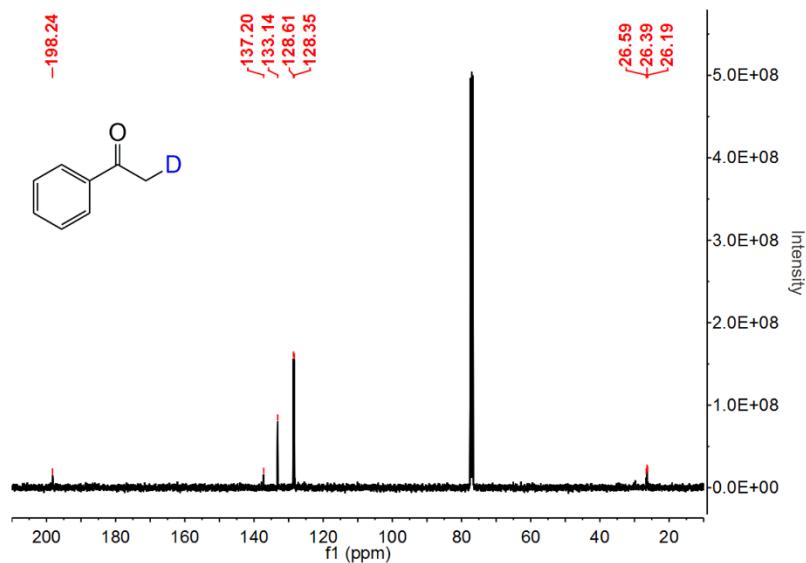


Figure S27. ¹³C NMR of product 2k. ¹³C NMR (400 MHz, CDCl₃): δ=198.2, 137.2, 131.1, 128.6, 128.4, 26.4, 26.2.

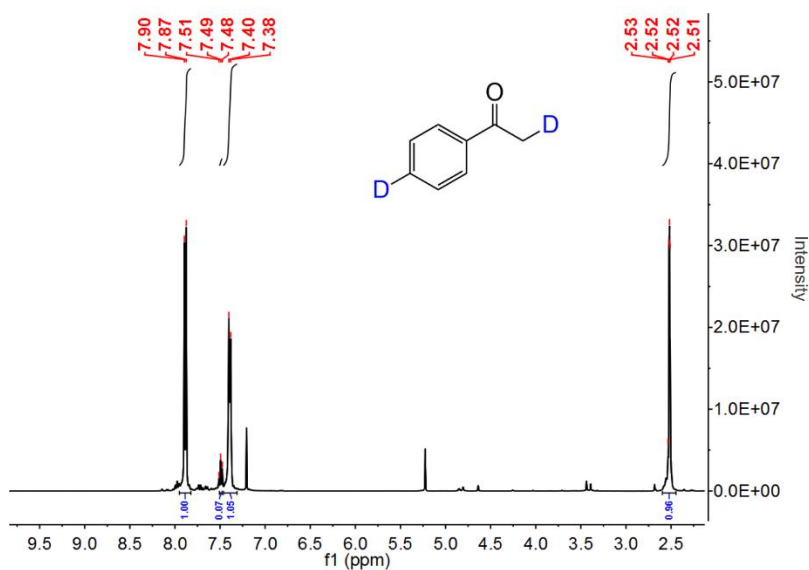
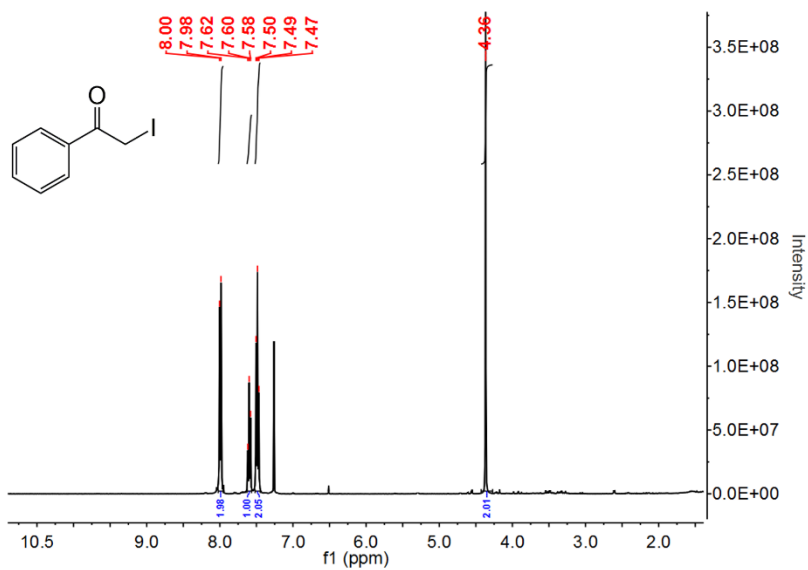
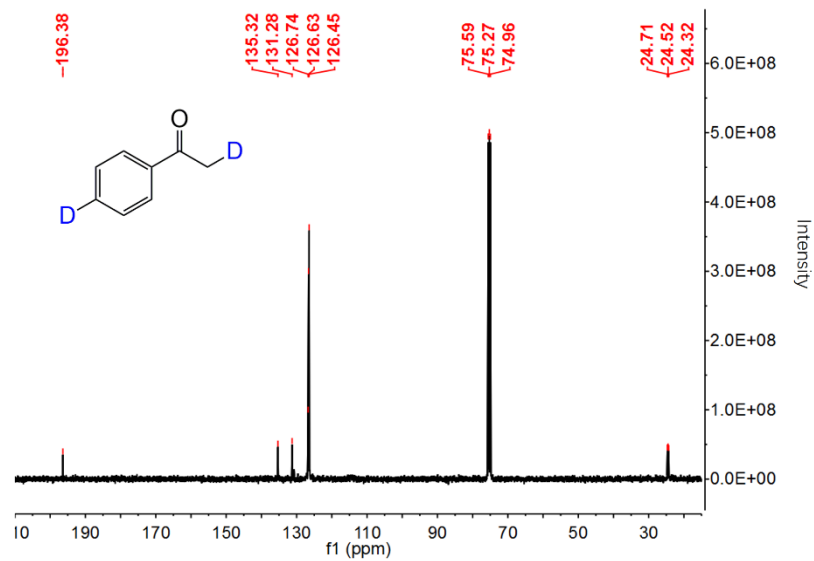


Figure S28. ¹H NMR of product 2l. Deuterated ratio=86%, ¹H NMR (400 MHz, CDCl₃): δ=7.90-7.87 (d, 2H), 7.51-7.48 (m, 0.14H), 7.40-7.38 (d, 2.1H), 2.53-2.51 (m, 1.92H); HRMS (EI) 122.0696, theoretical value for C₈H₆D₂O 122.0695.



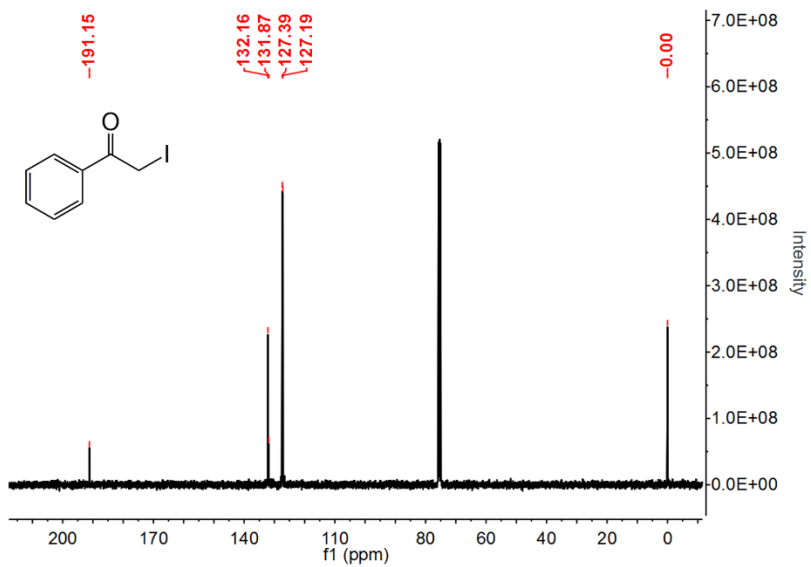


Figure S31. ¹³C NMR of substrate 2k.

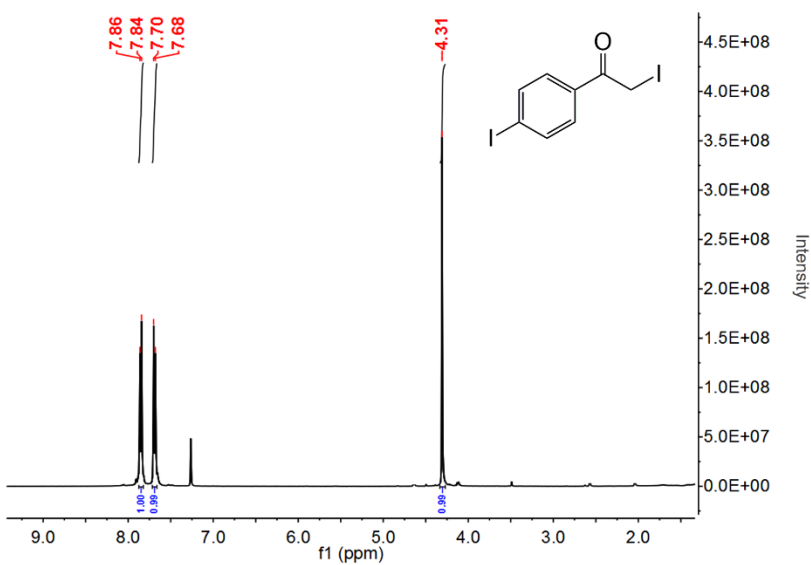


Figure S32. ¹H NMR of substrate 2l.

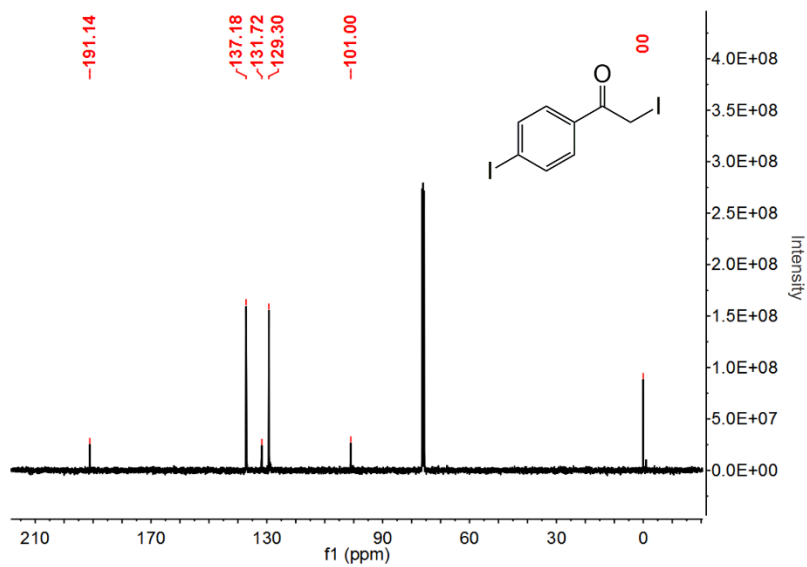


Figure S33. ^{13}C NMR of substrate 2l.

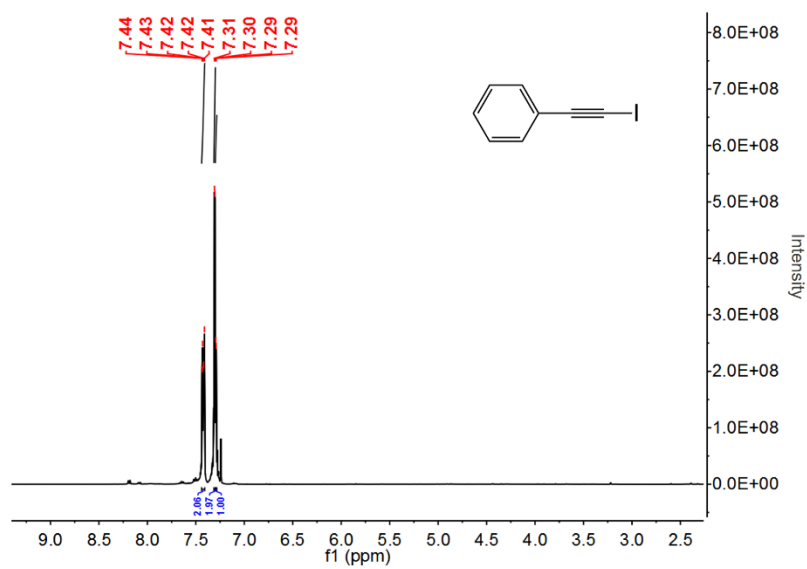


Figure S34. ^1H NMR of substrate 2m.

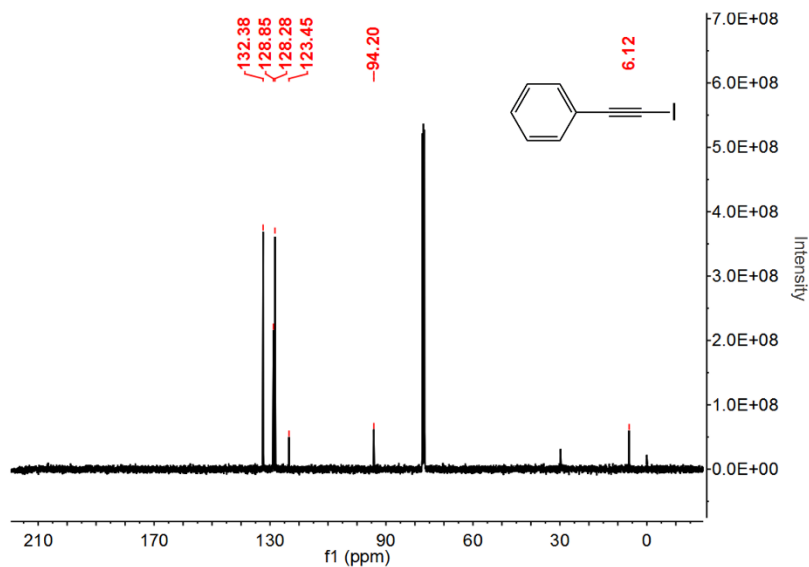


Figure S35. ^{13}C NMR of substrate 2m.

Table S1. Zeta potentials of Au colloid, CdS and APTMS modified CdS.

Substance	Au colloid	CdS	CdS-APTES
Zeta potential	-23.8 mV	-19.3 mV	14.1 mV

Table S2. The fitting parameters for the PL decay curves of the catalysts.

Sample	A_1	A_2	A_3	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ (ns)
CdS	0.117	0.011	--	1.1581	8.886	--	4.40
Au/CdS	0.087	0.089	0.046	0.6866	2.3057	9.2829	6.5

Table S3. Control experiments on the photocatalytic HDI.^a

Entry	Catalyst	Loading	Additive	t (h)	Conversion	GC yield
1	Au/CdS	5 mg	Na ₂ SO ₃	0.5	> 99%	> 99%
3	CdS	5 mg	Na ₂ SO ₃	0.5	5.6%	5.6%
4 ^b	Au/CdS	5 mg	Na ₂ SO ₃	0.5	trace	trace
5 ^c	Au/CdS	5 mg	Na ₂ SO ₃	0.5	trace	trace
6	--	--	Na ₂ SO ₃	0.5	trace	trace
7	Au/CdS	5 mg	--	0.5	trace	trace

a. Standard conditions: 4-iodoanisole (0.1 mmol), Au/CdS (5.0 mg), Na₂SO₃ (0.2 M), CH₃CN/H₂O (2.5 mL/2.5 mL), λ >400 nm, irradiation time 30 min, r.t.. b. in the dark. c. 60 °C, in the dark.

Table S4. Comparison of different sacrificial reagents for hydrodehalogenation and deuteration.

Sacrificial reagent	Na ₂ SO ₃	EtN ₃	EtOH	Na ₂ S	Lactic acid	Na ₂ SO ₃	Na ₂ SO ₃
Hydrogenation yield ^a	> 99%	> 99%	5%	49%	4%	83% ^b	88% ^c
Deuteration yield	> 99%	> 0%	0%	49%	0%	--	--

a. Standard conditions: 4-iodoanisole (0.1 mmol), Au/CdS (5.0 mg), Na₂SO₃ (0.2 M), CH₃CN/H₂O (D₂O) (2.5 mL/2.5 mL), λ >400 nm, irradiation time 30 min (1 h), r.t.. b. Na₂SO₃ (0.1 M). c. Na₂SO₃ (0.05M).

Table S5. Dissociation energy of C-X bond in aryl halide.

C-X bond	Ar-I	Ar-Br	Ar-Cl
Bond energy	67.4	80.4	97.1

REFERENCES

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- (3) Szell, P. M. J.; Dragon, J.; Zablony, S.; Harrigan, S. R.; Gabidullin, B.; Bryce, D. L.; Mechanochemistry and Cocrystallization of 3-Iodoethynylbenzoic Acid with Nitrogen-Containing Heterocycles: Concurrent Halogen and Hydrogen Bonding. *New J. Chem.* **2018**, *42*, 10493–10501.